

UNIVERSITE DE GENEVE
Section de chimie
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**1-AND 2-PHENYL-3-ACETYL-1-CYCLOPENTENES
AND 1-PHENYL-5-ACETYLBICYCLO [2.1.0] PENTANES :
PHOTOCHEMISTRY AND THERMAL REARRANGEMENTS**

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présentée à la Faculté des sciences de l'Université de Genève
pour obtenir le grade de docteur ès sciences, mention sciences chimiques

par

TEGMO-LARSSON Inga-May

citoyenne de la Suède

Thèse No 1772

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La Faculté des sciences, sur le préavis de Messieurs K. Schaffner, professeur ordinaire et directeur de thèse, C.W. Jefford, professeur ordinaire et J. Kossanyi, docteur ès sciences (Université Pierre et Marie Curie, Paris), autorise l'impression de la présente thèse, sans exprimer d'opinion sur les propositions qui y sont énoncées.

Genève, le 6 octobre 1976

Le Doyen :
Jean Muller

Thèse No 1772



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I owe special thanks to Mrs. Debi Marti for her assistance in typing this thesis.

to the memory of my father

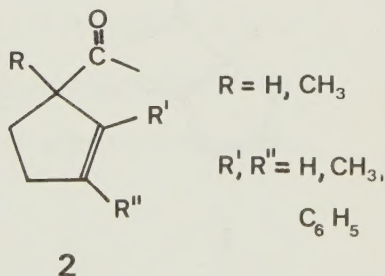
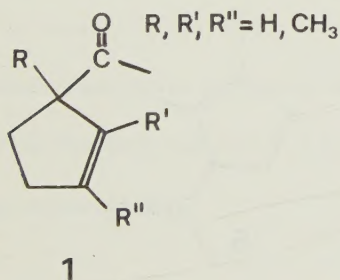
CONTENTS

1.	The 1,3-Acyl Shift and the Triplet-sensitized Oxa-di- π -methane Rearrangement of β, γ -Unsaturated Ketones	5
1.1	The 1,3-Acyl Shift	6
1.2	The Nature of the Reactive Singlet and Triplet States	12
1.3	The Mechanism of the ODPM Rearrangement	22
1.4	The Photochemistry of Acetylphenylcyclopentenenes	29
1.4.1	The Synthesis of the Acetylphenylcyclopentenenes	29
1.4.2	The UV Absorption Spectra of Acetylphenylcyclopentenenes	36
1.4.3	Direct Irradiation of 1-Phenyl-3-acetyl-1-cyclopentene (68)	41
1.4.4	Triplet Sensitization of 1-Phenyl-3-acetyl-1-cyclopentene	49
1.4.4.1	Preparative Experiments and Product Analysis	49
1.4.4.2	Identification of the Reactive Triplet State of 68	60
1.4.5	Preliminary Photolysis of Other Acetylphenylcyclopentenenes	65
2.	The Thermal Isomerization of 1-Phenyl-5-acetylbicyclo-[2.1.0]pentane	69
3.	Appendix: Asymmetric Induction in Triplet Sensitization	80
3.1	Synthesis of an Optically Active Indanone Sensitizer	82
3.2	Preliminary Sensitization Experiments	91
4.	Experimental Part	93
4.1	General Remarks	93
4.2	Synthesis of the Acetylphenylcyclopentenenes 68, 69, 75, 83 and 84	94

4.3	Direct Irradiation of the Acetylphenylcyclopentenes	106
4.3.1	Qualitative Irradiation of <u>68</u> , <u>69</u> , <u>75</u> and <u>84</u>	106
4.3.2	Preparative Irradiation of <u>68</u> and <u>69</u>	106
4.3.3	Synthesis of 1-Phenyl-1-acetylcyclopentane (<u>93</u>)	107
4.3.4	Photolysis of <u>92</u>	108
4.3.5	Preparation and Irradiation of <u>92-d₃</u>	109
4.4	Triplet Sensitization of the Acetylphenylcyclopentenes <u>68</u> , <u>69</u> , <u>75</u> , <u>83</u> and <u>84</u>	110
4.4.1	Sensitized Irradiations	110
4.4.2	Photoproducts	112
4.4.3	Irradiation of <u>98a</u> and <u>98b</u>	112
4.4.4	Synthesis of <u>98a</u> and <u>98b</u>	113
4.4.5	Quantum Yield Measurements for <u>68</u>	115
4.5	Emission Spectroscopy and Quantum Yields of Phosphor- escence of 1-Phenyl-3-acetyl-1-cyclopentene (<u>68</u>) and 1-Phenylcyclopentene (<u>91</u>)	116
4.6	Thermolysis of 1-Phenyl-5-acetylbicyclopentanes (<u>98a,b</u>)	117
4.7	Synthesis of (1S, 4R, 4aS, 9aS)-(-) and (1R, 4S, 4aR, 9aR)- (+)-1,2,3,4,4a,9a-Hexahydro-1,4-methanofluoren-9-one (<u>139</u>)	118
4.8	Sensitization Experiment with (1S, 4R, 4aS, 9aS)-(-)- 1,2,3,4,4a,9a-Hexahydro-1,4-methanofluoren-9-one (<u>139</u>)	123
5.	Summary	124
6.	Résumé	126
7.	Literature References	128

1. The 1,3-Acyl Shift and the Triplet-sensitized Oxa-di- π -methane Rearrangement of β,γ -Unsaturated Ketones

Photochemical excitation causes homoconjugated β,γ -unsaturated ketones to react via two main routes^{1,2,3} which in most cases originate from different excited states. Photoisomerization to a new β,γ -unsaturated ketone by a 1,3-acyl shift occurs upon direct irradiation. Triplet sensitization involves a formal 1,2-acyl shift and formation of a cyclopropyl ketone, which may be thermally unstable and rearrange back to β,γ -unsaturated ketone. The detailed mechanism of these rearrangements and the electronic configuration of the reactive triplet state in the so called oxadi- π -methane (ODPM) rearrangement⁴ are still a matter of current debate. The principal aim of the present work has been directed towards the identification of the reactive triplet state of a ketone undergoing an ODPM rearrangement. In the following literature reviews of specific aspects of β,γ -unsaturated ketone photochemistry, the discussion will, whenever possible, focus on results obtained with 1-acetyl-2-cyclopentenones (**1**), work carried out by Gonzenbach⁵.

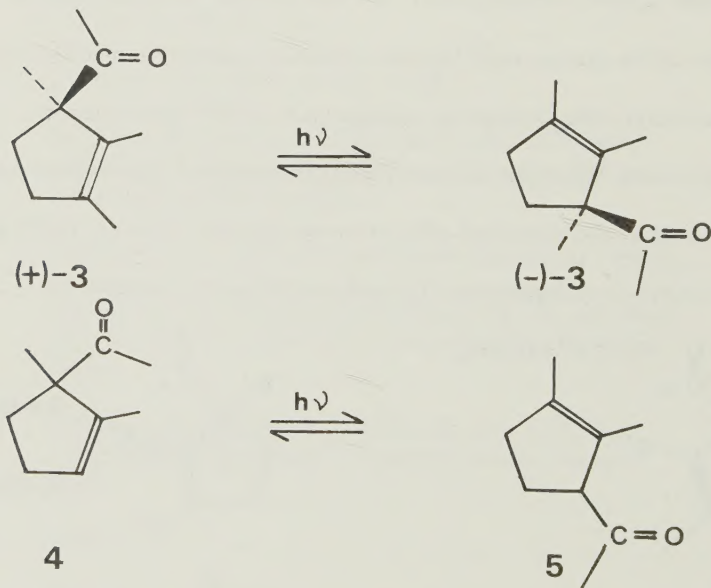


The reason for this preference is twofold: 1) the photochemistry of this class of compounds has been investigated on a relatively broad basis. A discussion of the results obtained, combined with appropriate references to findings with other

β,γ -unsaturated ketones, provides a convenient access to all relevant informations in this field; 2) the experimental work of this Thesis concerns phenyl analogues of compounds 1, i.e. 2.

1.1 The 1,3-Acyl Shift

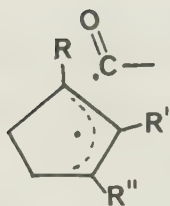
The direct irradiation of, e.g., (+)-3⁶ and 4⁵ leads to photostationary equilibria owing to racemization of 3 and the formation of the isomeric ketone 5, respectively.



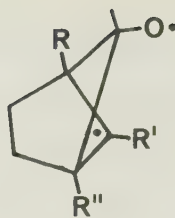
The structural change involved in $\underline{4} \rightleftharpoons \underline{5}$ as well as kinetic studies involving (+)-3 and deuterium-labelled rac-3 unequivocally showed that a 1,3-allylic shift of the

acetyl group constitutes the only mechanistic path of this reaction. Experiments with mixtures of appropriate deuterium-labelled ketones 3 showed furthermore that the reaction is completely intramolecular.

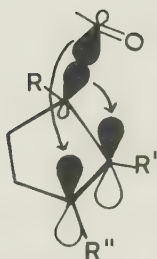
Three different mechanistic routes may be taken into consideration: 1) α -cleavage to radical pair 6 which recombines prior to diffusion. This mechanism is at first sight the most plausible one in view of the fact that ketones quite generally undergo such a photochemical cleavage with great ease. In the case of an allylic double bond the α -cleavage could be expected to be particularly facile. Indeed, α -cleavage is obviously an efficient competitive reaction in these compounds, and radical combination products such as the cyclopentenyl dimer and biacetyl are formed. However, a CIDNP showed a negligible polarization in starting material and in 1,3-rearranged product, which eliminates recombination of both geminate pair and free radicals for the acetyl migration process. 2) Formation of a 1,3-bridged diradical intermediate (7) may be envisaged as another stepwise mechanism. This route is not excluded for compounds such as 3 and 4 but is hardly applicable to many other compounds showing the same type of photoreaction (e.g., 9) for structural constraints. 3) The presently most convincing mechanism is a concerted suprafacial 1,3-sigmatropic shift (cf. 8), a photochemically allowed ($\sigma_S^2 + \pi_S^2$) process in terms of orbital symmetry conservation rules.



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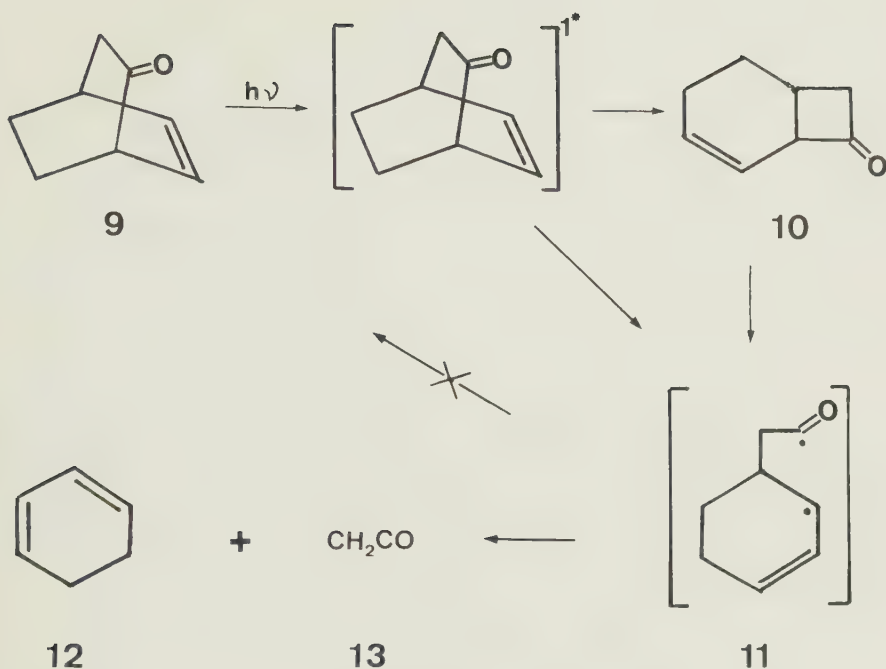


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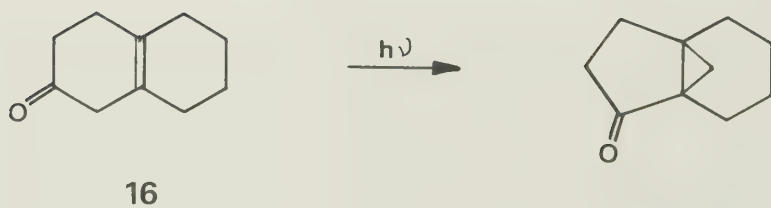
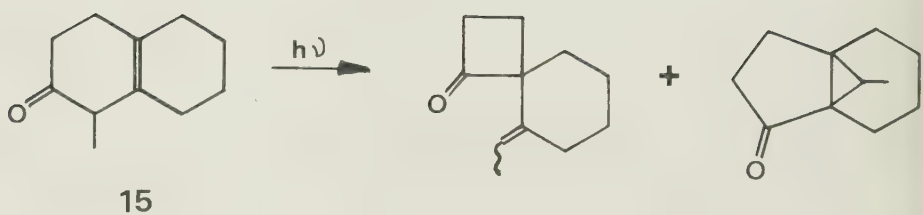
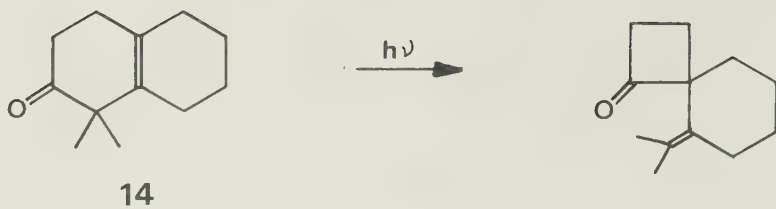


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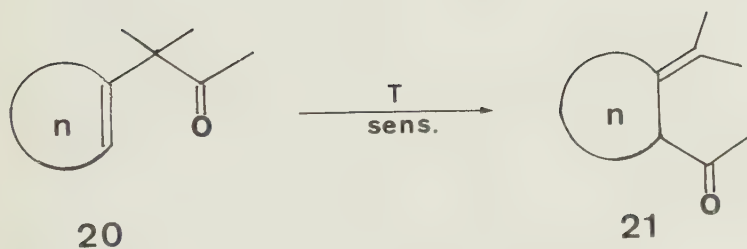
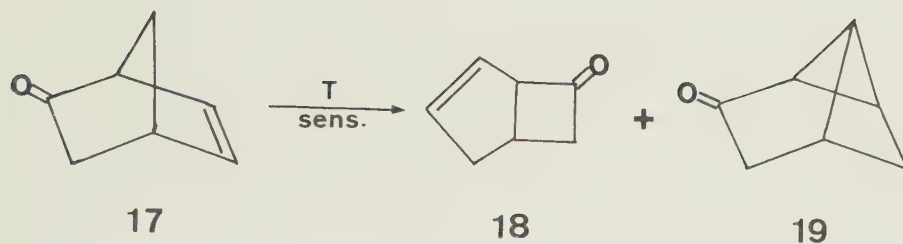
The CINDP results mentioned above may be taken as evidence in favor of either mechanism 2 or 3. Taking into account the particularly unfavorable steric situation in ketone 9 for path 2, the results reported by Givens⁷ provide strong support for the concertedness of the 1,3-acyl shift. Thus, 9 on direct irradiation furnishes both the isomer 10 and the fragmentation products 12 and 13. The latter obviously arise from an α -cleavage to the 1,4-diradical intermediate 11 and subsequent fission. The same fragmentation is also observed from 10 whereas the reverse rearrangement to 9 has not been detected. This finding is taken to exclude a stepwise mechanism for the 1,3-acyl shift involving an intermediate common with the fragmentation path.



The singlet multiplicity has been assigned to the 1,3-shift by all authors in the past on the basis that the reaction is normally observed only upon direct irradiation and is not quenchable. Triplet sensitization, furthermore, gives the ODPM rearrangement and other triplet reactions instead. It is therefore evident that S_1-T_1 intersystem crossing is inefficient in these β,γ -unsaturated ketones. Cases are described, however, where direct irradiation affords either a mixture of 1,3-acyl shift and ODPM rearrangement products or only the latter. This is due to competition between α -cleavage and intersystem crossing for geometrical and structural reasons. Engel⁸ has found this trend in the octalones 14, 15 and 16. Quenching of the conversion to cyclopropyl ketone, $\phi_{isc} = 0,5$ and $\phi_{sens} = \phi_{direct}$ are data which clearly establish the intersystem crossing to a triplet state for the ODPM rearrangement in this series.



On the other hand, examples of 1,3-acyl migration have been encountered also in sensitized photolyses, e.g., $\underline{17} \longrightarrow \underline{18} + \underline{19}$ ⁹ and $\underline{20} \longrightarrow \underline{21}$ ¹⁰.



$n = 4\text{- and } 5\text{-membered rings}$

The singlet assignment to the 1,3-acyl shift is presently being debated^{11,12}.

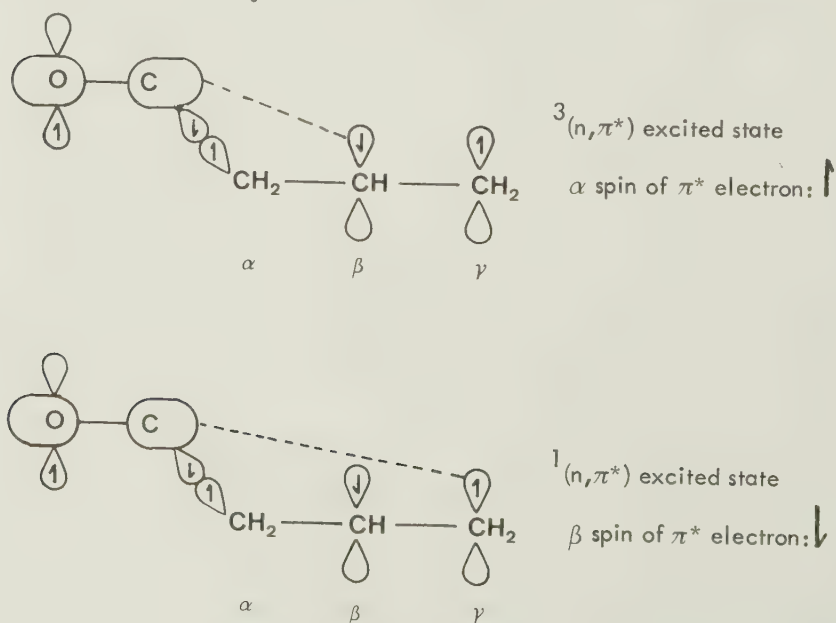
The proposal has been forwarded that the reaction may just as well occur from the second triplet state, presumably n, π^* in nature. In other words, intersystem crossing would then be efficient on the level $S_1(n, \pi^*) \rightarrow T_2(n, \pi^*)$, and internal conversion $T_2 \rightarrow T_1$ would be prevented by more efficient reaction from T_2 (Note that this configurational preference in intersystem crossing does not follow the spin-orbit coupling rules. However, precedent for such "abnormal" behaviour has recently been found by ourselves^{3,13} in a study of 1-indanones).

In the following discussion (chapter 1.2) the reactive state for the 1,3-acyl shift will be termed the "singlet" excited state in conformity with the literature and disregarding the above-mentioned debate on the true multiplicity.

1.2 The Nature of the Reactive Singlet and Triplet States

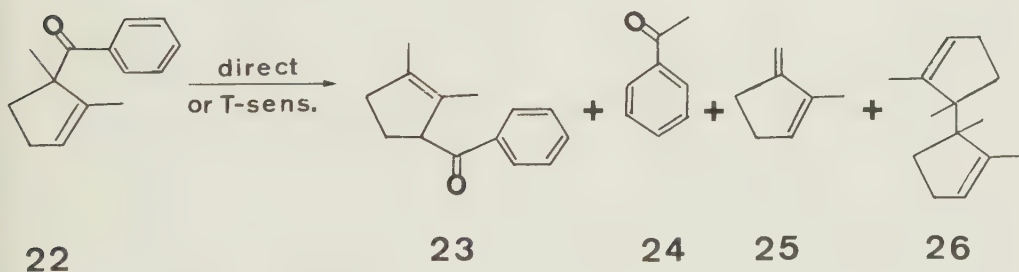
The electronic configuration of the reactive triplet in the ODPM rearrangement has been the subject of several theoretical treatments and experimental studies employing emission spectroscopy.

Schuster, Underwood and Knudsen¹⁴ proposed that both the triplet 1,2- and the singlet 1,3-acyl shift involve the n, π^* configuration. Their rationale was based on spin density distribution where the spin polarization exerted on the σ frame and the olefin π bond primarily originates from interaction with the singly occupied p_y orbital. Introduction of the $\pi^*_{C=O}$ electron of α spin (triplet) leads to bonding with C_β and 1,2-acyl migration. Alternatively, the β spin (singlet) is set for bonding with C_γ resulting in 1,3-acyl migration (Scheme 1).



Scheme 1

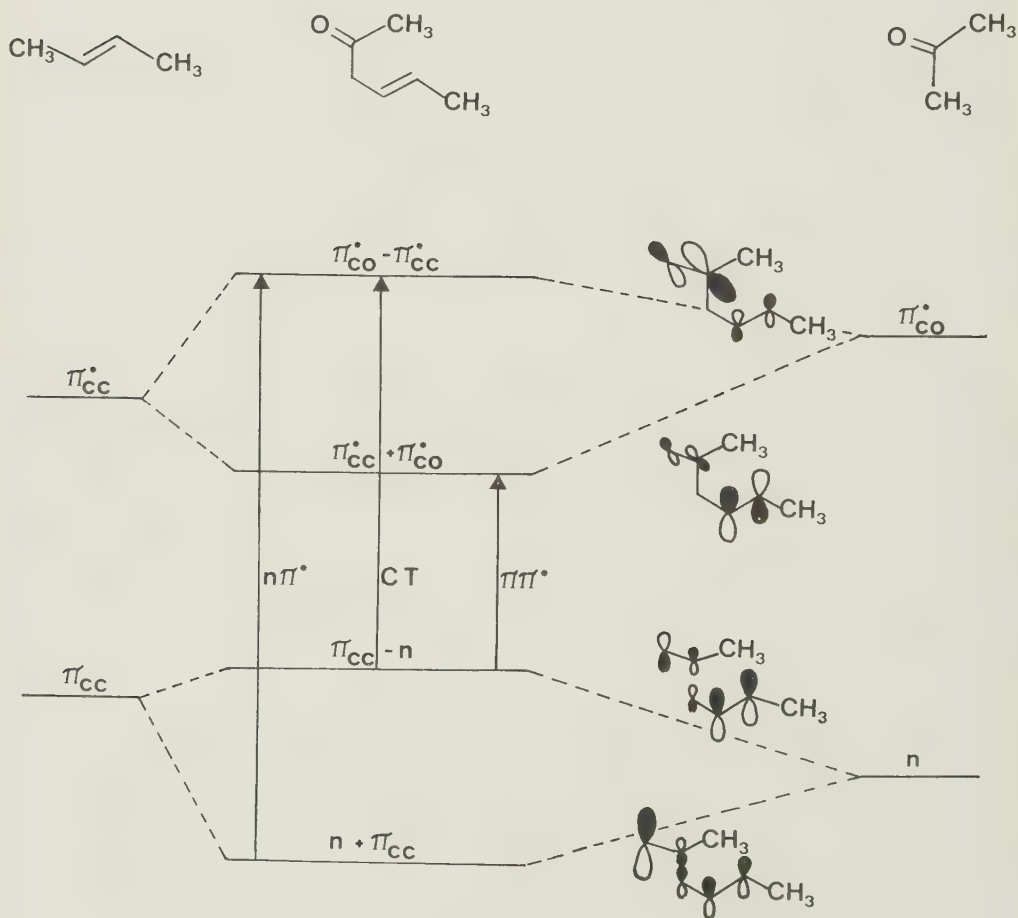
This explanation, however, does not rationalise the observation that n, π^* triplet states of β, γ -unsaturated ketones may preferentially undergo α -cleavage rather than ODPM rearrangement. Thus, the arylketone 22⁵ does not give any cyclopropyl ketone (ODPM product) either on triplet-sensitized or direct irradiation. The lowest triplet state of 22 is of n, π^* nature as shown by phosphorescence, which is similar in energy, spectral shape and lifetime ($\tau_{ph} \sim 5,5$ ms) to the phosphorescence of acetophenone, the parent chromophore. The triplet reaction of 22 was found to be α -cleavage, followed by radical recombination and disproportionation processes ($\rightarrow$ 23 - 26).



A different theoretical approach was chosen by Houk¹⁵ using a molecular orbital model. The eigenvectors and eigenvalues were obtained by CNDO calculations, and in combination with configuration interaction these calculations yielded the transition energies and the relative state energies. This approach is based on differences in the electronic configuration of the excited singlet and triplet states.

The model used takes into consideration the homoallylic conjugation of β, γ -unsaturated ketones at optimum geometry. The molecular orbitals of trans-4-hexen-

2-one were thus obtained from mixing the HOMO's and LUMO's of acetone and trans-2-butene as shown in the scheme below.

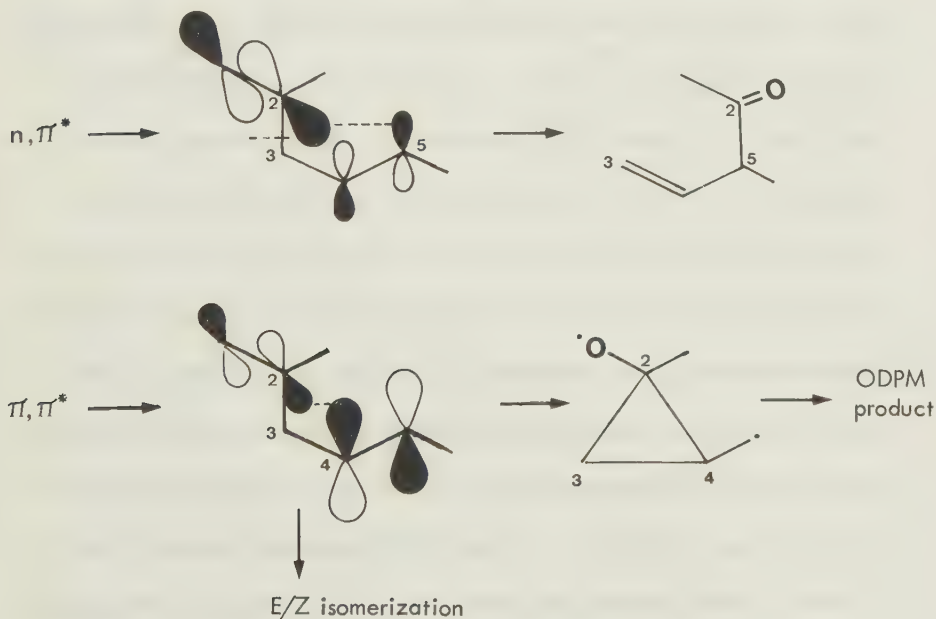


Scheme 2

configuration S_1 $^1n, \pi^*$ 54% ($n + \pi_{cc} \rightarrow \pi_{co}^* - \pi_{cc}^*$) + C.T. 32% ($\pi_{cc} - n \rightarrow \pi_{co}^* - \pi_{cc}^*$)
 configuration T_1 $^3\pi, \pi^*$ 76% ($\pi_{cc} - n \rightarrow \pi_{cc}^* + \pi_{co}^*$)

The lowest excited singlet state, $^1(n;\pi^*)$, involves removal of the C_2-C_3 bonding character and introduction of a C_2-C_5 bonding effect. In other words, α -cleavage and/or C_2-C_5 bonding leading to the 1,3-shift should arise from an n,π^* state. One may conclude that $^1n,\pi^*$ and $^3n,\pi^*$ have similar (anti)bonding properties and thus should show similar reactions. This in fact is confirmed by the similar results of the direct and sensitized irradiation of the β,γ -unsaturated aryl ketone 22 (see page 13).

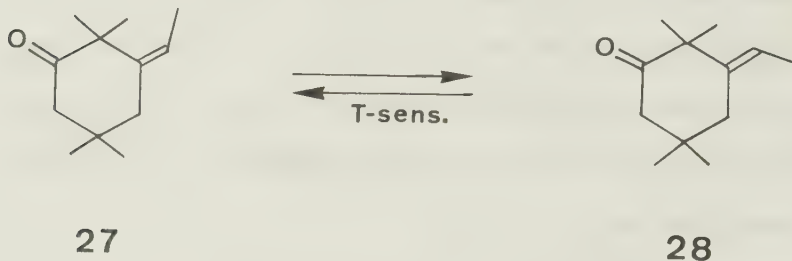
The lowest excited triplet state, $^3(\pi;\pi^*)$, exhibits a C_2-C_4 bonding effect and little weakening of the C_2-C_3 bond. This could result in a diradical formation of the type proposed for the ODPM rearrangement.



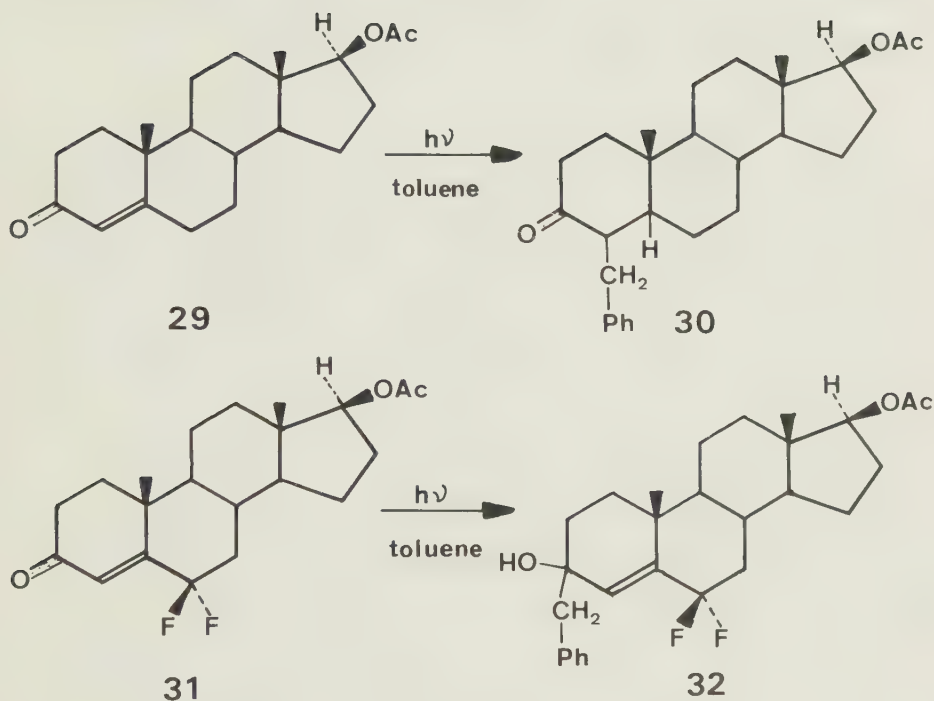
Scheme 3

Another feature of the C_2-C_4 bonding effect is a weakening of the $C=C$ bond,

which may provide a mechanism for the E/Z double-bond isomerization competing with the ODPM rearrangement (cf. 27→28)¹⁶.

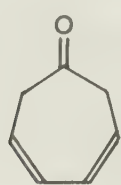


It may appear obvious that the electronic configuration of a reactive enone triplet may be determinant in the course of the reaction. Yet, it is difficult to find in the literature examples which are experimentally thoroughly documented and show the point in question. Among the relatively well investigated cases is that of the compound pair testosterone and 6,6-difluorotestosterone¹⁷. The lowest-lying triplet of these two compounds are clearly characterized by phosphorescence to be π, π^* and n, π^* in nature, respectively. This difference is reflected in their specifically different photochemical behaviour. Irradiation in toluene results in clean photoreaction of both ketones, 29 leading to the saturated α -benzyl ketone 30, and 31 giving exclusively the allylic tertiary benzyl alcohol 32. The structure of the latter product is only explicable by a primary hydrogen abstraction on oxygen (which is electron deficient in the n, π^* state) whereas product 30 must result from a C_β abstraction of hydrogen suggesting a π, π^* reactive state.



If the correlation of electronic configuration and reactivity in this example may still need further refinement, especially in terms of unified reaction conditions for all observables, a search for similar illustrations in the field of β,γ -unsaturated ketones unveil even less satisfactory examples. The photochemistry of 3,5-cycloheptadienones may serve as an illustration. The triplet sensitized photolysis leads to the cyclization of the diene moiety in the case of the parent compound (33 $\rightarrow$ 34)¹⁸, and to an ODPM-type rearrangement in the case of the 2,7-tetramethyl homolog (35 $\rightarrow$ 36)¹⁸. Clearly the result (33 $\rightarrow$ 34) is highly suggestive of a reactive state which involves the π,π^* nature

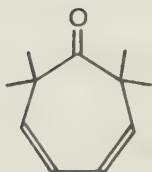
of the diene chromophore. An extrapolation to a configurational assignment to the reactive triplet in 35 would, however, appear hasardous.



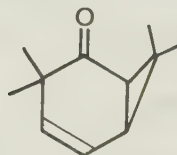
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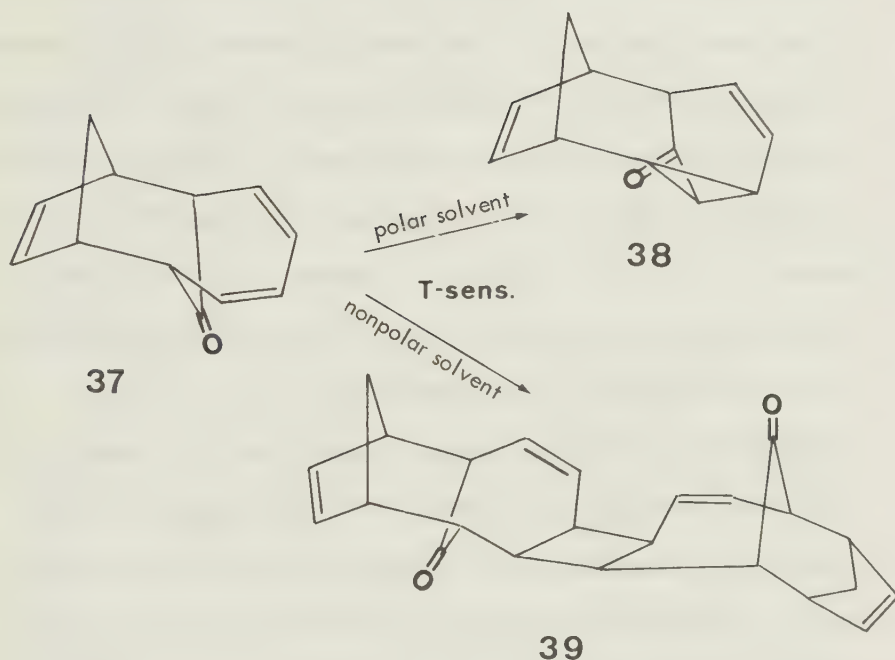


35



36

A similar indication of diene π, π^* reactivity¹⁹ may be seen in the triplet dimerization of 37 which predominates in non-polar solvent. A triplet ODPM rearrangement is observed in the same ketone when the reaction is carried out in a polar solvent. On the basis of CNDO-CI calculations and the observation of an unusual solvent-dependent charge transfer shift it has been argued that the $^3(n, \pi^*)$ state should be responsible for the rearrangement. However, a definitive correlation of electronic configuration and reactivity of triplet 37 warrants more convincing experimentation (in the opinion of this author).

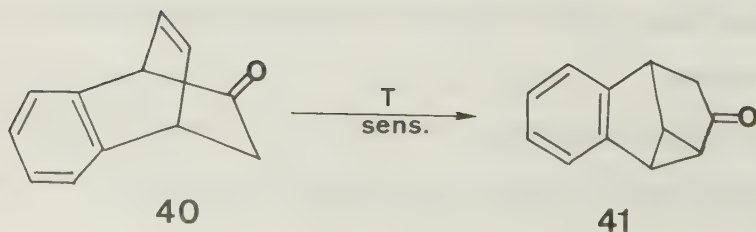
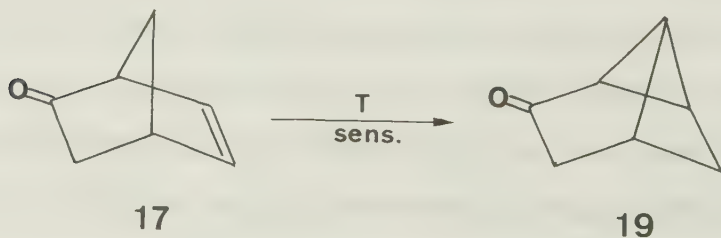


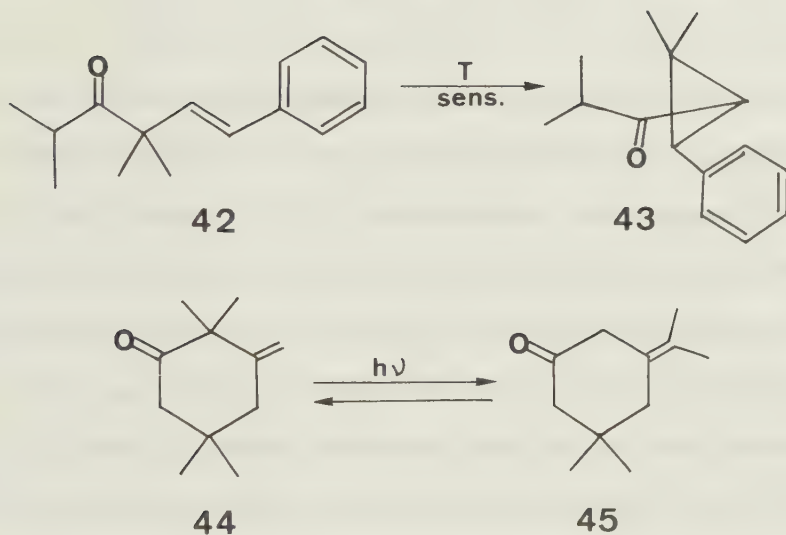
As has been briefly mentioned above phosphorescence constitutes the method of choice for the study of the electronic configuration of a triplet state. Unfortunately this tool does not seem to be generally applicable to β,γ -unsaturated ketones. There has been a report in the literature on phosphorescence assigned to ten β,γ -unsaturated ketones²⁰. However, the origin of some of these emissions has since been shown to stem from impurities, and appears doubtful in at least some other examples.

Engel has demonstrated that compounds 17 and 44 definitely do not phosphoresce⁹ and the same finding has recently been established beyond doubt for 1,2-dimethyl-

1-acetylcyclopentene (1)²¹. Among the remaining examples reported as phosphorescing, the two following may deserve critical comment. Benzobicyclo[2,2,2] octadienone (40) rearranges to 41 on sensitization with acetophenone ($E_T = 74$ kcal/mol) and acetone ($E_T = 80$ kcal/mol) whereas benzophenone ($E_T = 68$ kcal/mol) is ineffective as a sensitizer²². This places the triplet energy of 40 close to 70 kcal/mol. The reported 0-0 triplet energy of 60.9 kcal/mol appears to be highly doubtful in view of the sensitization results and the nature of the chromophoric partial structures and conformational rigidity of the compound.

Furthermore, the absence of any phosphorescence in styrene is attributed to efficient deactivation of the triplet state by double-bond isomerization. Yet, compound 42 is supposed to exhibit a phosphorescence with an origin at 68,8 kcal/mol. The doubts on the validity of this emission are still further accentuated by the fact that Dauben⁴ observed the ODPM rearrangement for (42 $\rightarrow$ 43) with α -acetonaphthone ($E_T = 56$ kcal/mol) as a triplet sensitizer.

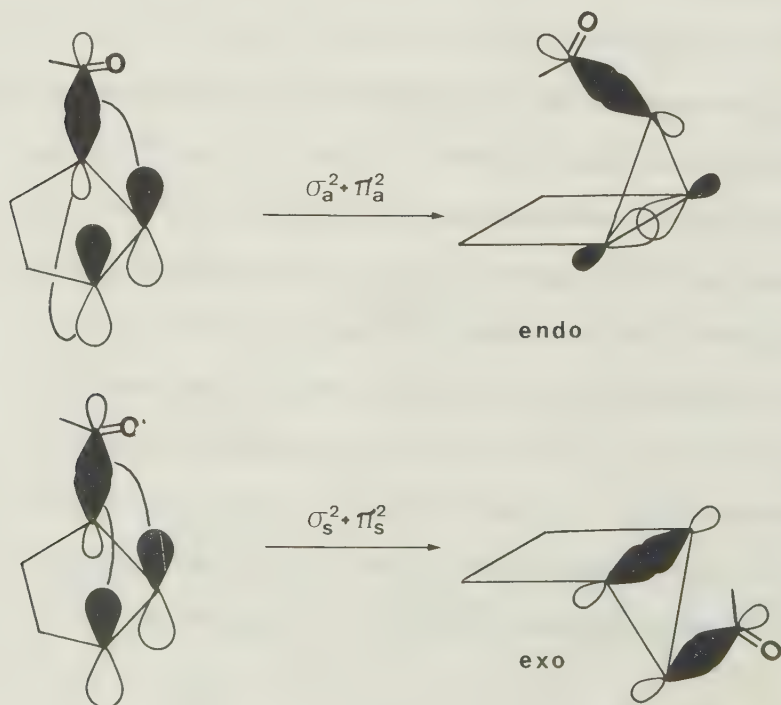




A lack of intersystem crossing in β,γ -unsaturated ketones may be explained by inefficient spin-orbit coupling between $^1n,\pi^*$ and $^3\pi,\pi^*$ states²³. Contrary to the case in α,β -unsaturated ketones, where the π^* orbital is the same for both states, the spin-orbit operator is small in nonconjugated β,γ -unsaturated ketones since the π^* orbital involved is different for the two states. There is at best a small amount of π^*_{cc} character in the n,π^*_{co} state (either by π^*_{cc} overlap with π^*_{co} or by $n,\pi^*_{co} - \pi_{cc}\pi^*_{cc}$ configuration interaction) and a small amount of π^*_{co} character in the $\pi_{cc}\pi^*_{cc}$ state. The rate constants for singlet-triplet intersystem crossing, k_{ST} , were found to be about 10^8 in β,γ -unsaturated ketones and about 10^{11} in α,β -unsaturated ketones.

1.3 The Mechanism of the ODPM Rearrangement

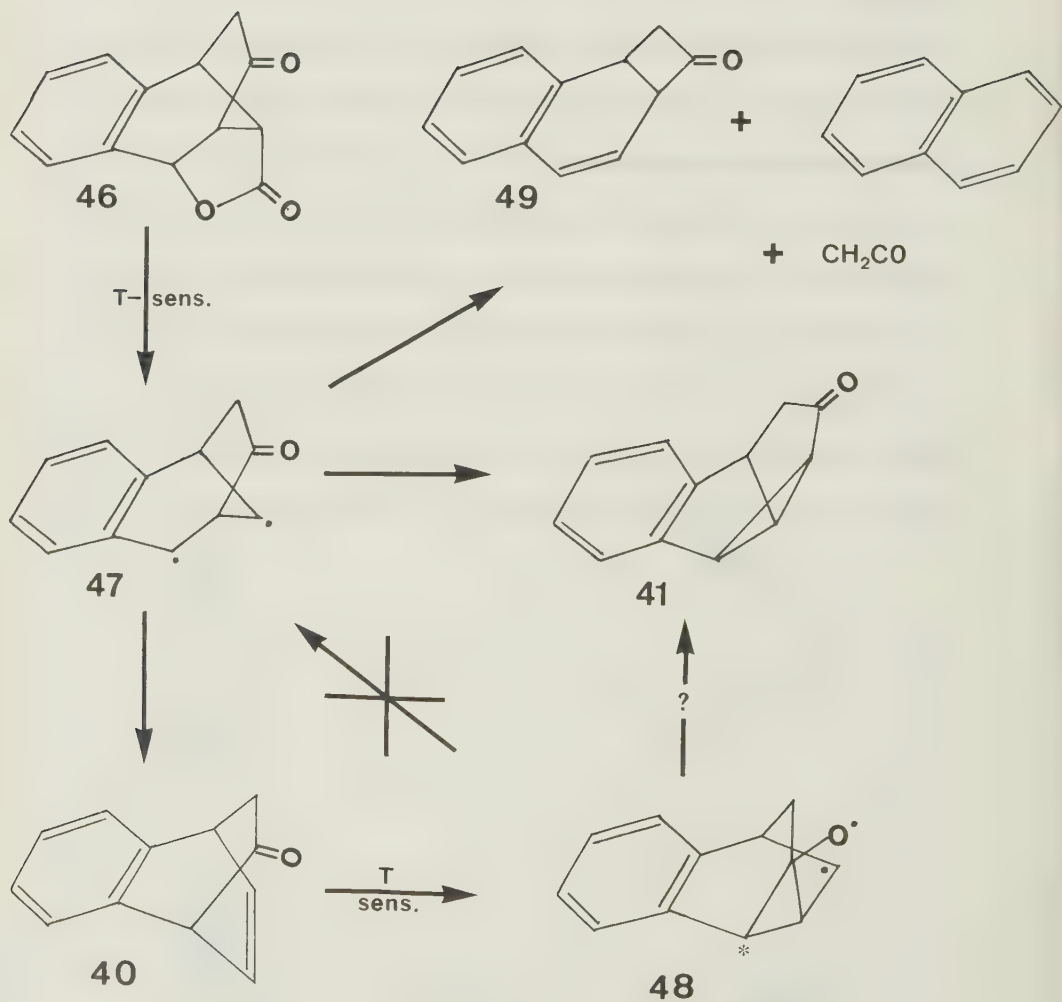
The reaction mechanism of the ODPM rearrangement is still equivocal. Both concerted and stepwise pathways have been postulated. The fully concerted process is interpreted as a symmetry-allowed ($\sigma_s^2 + \pi_s^2$) or ($\sigma_a^2 + \pi_a^2$) cycloaddition of the carbonyl- α -carbon bond and the β,γ -olefin bond. The doubly antarafacial path constitutes an anti-disrotatory process and the suprafacial alternative a syn-disrotatory mode. For stereoelectronic reasons the geometry of the s+s transition state is probably less favorable in general. But, in the case of the acetylcyclopentenones both would be required since both endo- and exo-stereoisomers are obtained. A stepwise mechanism is therefore just as likely.



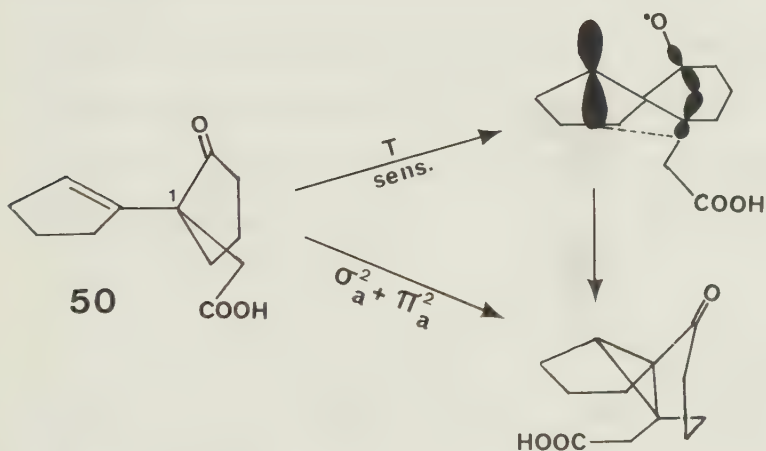
Scheme 4

Givens²² suggested a fully concerted reaction mechanism for the rearrangement of benzobicyclo[2,2,2]octadienone (40) based on the results of the sensitized rearrangement of 40 and the photodecarboxylation of the lactone 46 (Chart 1). Sensitization of the lactone gave 40, the ODPM rearrangement product 41, the cyclobutanone 49, naphthalene, and ketene. All these compounds can be formulated to arise from diradical 47, the obvious primary photoproduct. The cyclobutanone was, however, not formed upon the sensitized irradiation of 40 and consequently the authors exclude the 1,3-diradical 47 as a common intermediate for the two reactions. Rather, they postulate a concerted pathway for the ODPM rearrangement with the argument that the diradical 47 would be a mandatory intermediate in both the stepwise ODPM route and the path leading to cyclobutanone 49. However, 47 could possibly be avoided in the former process by a direct radical substitution at C* in intermediate 48.

Chart 1



The same author²⁴ claimed that the triplet rearrangement of 50 involves a concerted mechanism as well. This conclusion is based on the fact that the reaction occurs with ca. 90% inversion at C_1 . This foundation is inadequate because the two stepwise routes with inversion and with retention of configuration at C_1 involve diastereoisomeric conformations (of starting material) and structures (of the CO- C_β bonded intermediates), and the reaction must therefore be stereoselective.

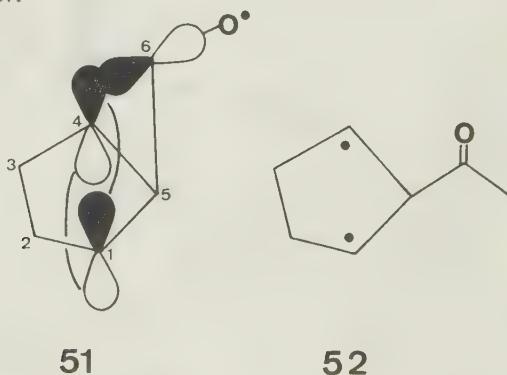


The majority of ODPM rearrangements, however, have been discussed in terms of a nonconcerted process via the cyclopropane carbonyl oxy diradical 51. This intermediate is in good agreement with the prediction from the theoretical calculations by Houk¹⁵ and Schuster¹⁴.

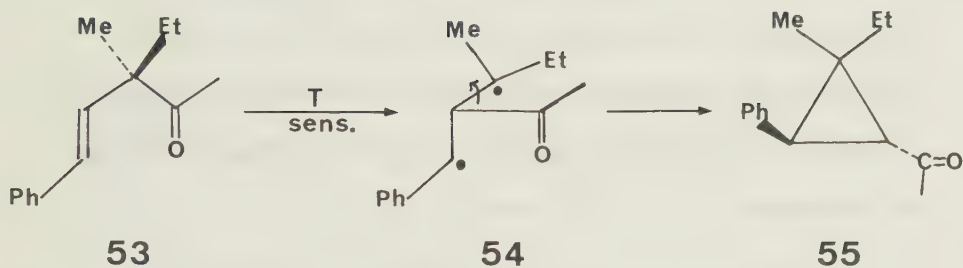
The initial step consists of bonding between the carbonyl carbon and C_β , followed by simultaneous anti- and/or syn-disrotatory cyclization and cleavage of the three-membered ring. In the case of the acetylcyclopentenones

the formation of endo- and exo-products with inversion and retention of C_α configuration, respectively, is thus explicable. The preference for the endo-isomer could derive from a better initial overlap between the backlobe at the C_1 orbital and the antilobe at C_4 and/or the requirement of least motion of the orbitals on the path to the transition state leading to full bonding.

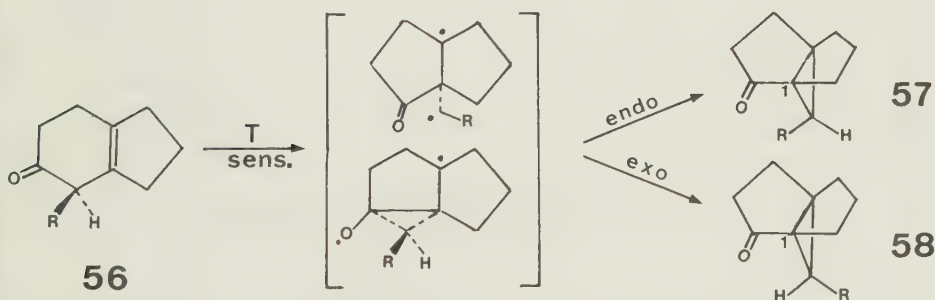
One may also consider a second localized diradical of type 52 by opening of the C_4-C_6 bond in 51. This type of diradical mechanism should also result in a kinetically controlled endo- and exo-product mixture of which the composition is difficult to predict.



Dauben²⁵ has recently carried out the sensitized irradiation of the optically active trans-3-ethyl-3-methyl-5-phenyl-4-penten-3-one (53). It results in the formation of a racemized ODPM rearrangement product which demonstrates the involvement of a stepwise mechanism via at least one diradicaloid intermediate like 54. The phenyl conjugation may have a stabilizing effect on the benzylic diradical here. Only the trans-isomer is formed, which could be due to steric hindrance in the cis-formation.

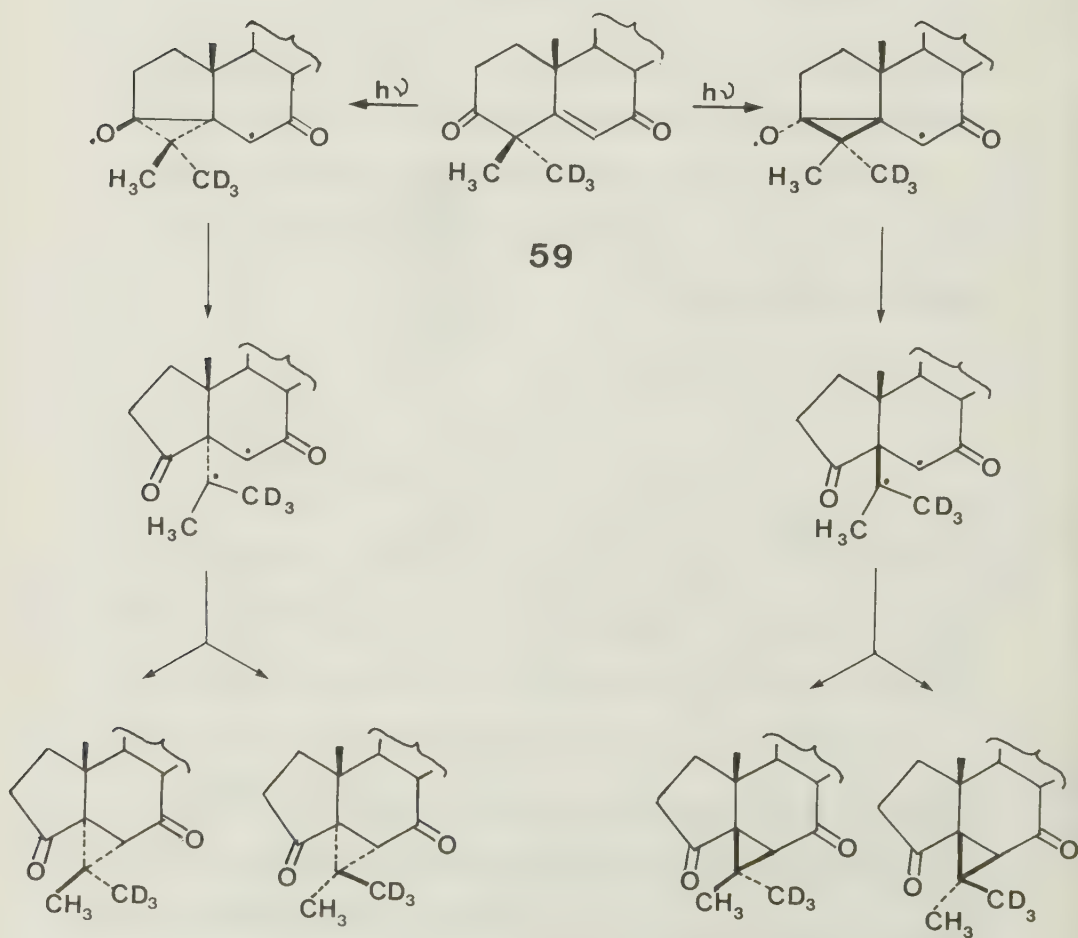


Proof for a stepwise mechanism involving intermediates of the same type as 51 and 52 has been reported by Winter and Schaffner²⁶ for the cyclohex-3-enone 56. The endo- and exo-products 57 and 58 show almost full retention of enantiomeric purity and they have identical C_1 configurations which constitutes evidence for the stepwise pathway.



An analogous pathway has been proposed for the rearrangement of the β, γ -unsaturated δ -dioxo steroid system 59²⁷ on direct irradiation at 254 nm, a wavelength which is not absorbed by the products under the reaction conditions. Complete scrambling of the CD_3 and CH_3 groups in the products is possible only under

conditions of 1,3-diradical formation, in which the isopropyl radical group can rotate around the angular bond prior to ring closure. This route could be the preferred one for the reasons which have already been mentioned for 54, namely the effect of radical resonance stabilization by a neighbouring π -system (here the 7-keto group).



1.4 The Photochemistry of Acetylphenylcyclopentenenes

The main topic of this part of the Thesis was now to incorporate into 3-acetyl-1-cyclopentene a chromophoric system which should allow an identification of the electronic nature of the triplet state responsible for the ODPM rearrangement. For this purpose the 1- and 2-phenyl-3-acetylcyclopentenenes 68, 69, 75, 83 and 84 were prepared. We expected the lowest-lying triplet state of these compounds to correspond closely to the relatively low-lying $^3(\pi, \pi^*)$ state of styrene with little perturbation by the carbonyl group. Moreover, twisting around the double bond is limited in the five-membered ring. Radiationless triplet deactivation should therefore be restrained in favor of emission at low temperature. As will be shown in the following chapters, these expectations were met by experiment.

1.4.1 The Synthesis of the Acetylphenylcyclopentenenes

(Charts 2 and 3) The aldehyde 61²⁸ was prepared by one-step reduction of 60²⁹ with DIBALH³⁰, and ketone 71 was obtained from the basic hydrolysis of 60 to acid 70 followed by treatment with methyl lithium³¹.

All the cyclopropyl acrylic esters, 62, (E)-63, (Z)-63, 72, (E)-77, (Z)-77, (E)-78 and (Z)-78, were obtained by a procedure described by Jorgenson³² who used the modified Wittig method of Wadsworth and Emmons³³.

Chart 2

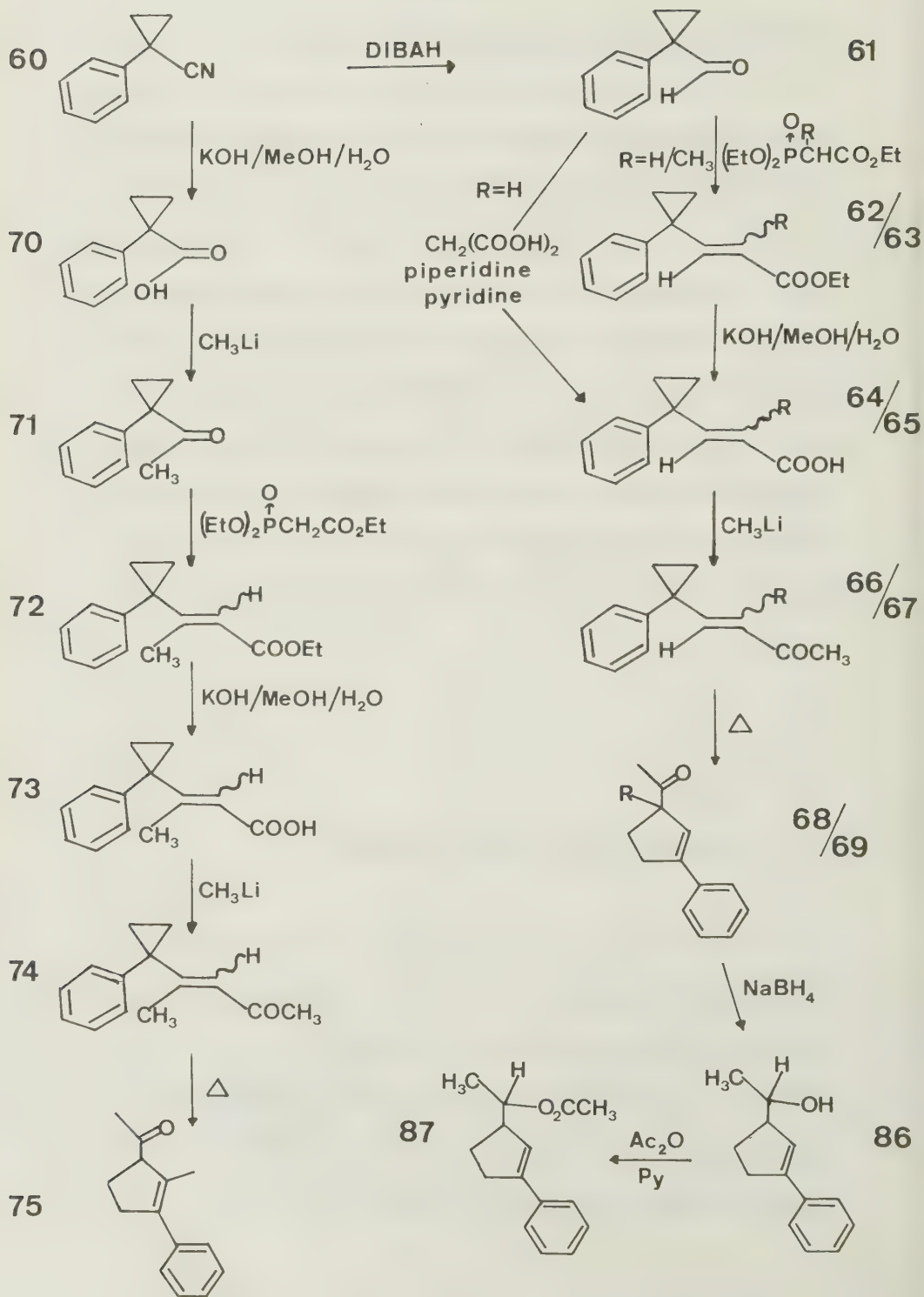
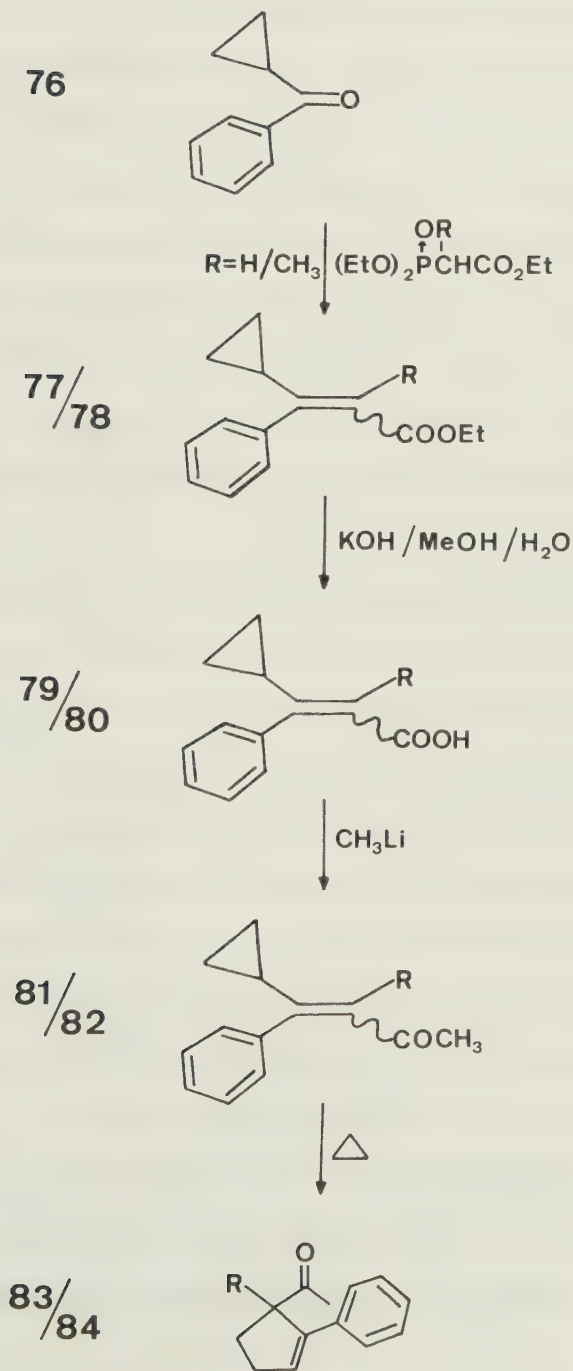


Chart 3



The diastereoisomeric ester composition obtained in these "Wittig" reactions strongly depended on the substitution pattern of the double bond. The Z-isomer appears to be formed only when the E-arrangement is sterically not strongly favored. Thus in the case of the disubstituted olefin and its tri-substituted β -methyl homolog 72 only the E-isomers were obtained. In the case of 63 in which either the carboethoxy or the α -methyl group is necessarily cis to the large phenylcyclopropyl substituent, both isomers are formed in similar proportions. E-Z mixtures are also obtained in the β -phenyl series 77 and 78. Here again one and two strong cis-interactions, respectively, can account for this result (note that both cyclopropyl and phenyl groups are assumed to be larger than methyl).

Examination of the UV absorption properties of the β -phenyl substituted cyclopropyl acrylic esters show a very small bathochromic or even hypsochromic shift in the E-isomers and a large hypsochromic effect in the Z-configuration compared to the parent methylated cyclopropyl acrylic esters^{34, 35}. Alternatively, taking the cinnamic esters as a basis for comparison the UV absorption is characterized by a large hypsochromic shift in all cases (see Table I).

These data can be rationalized by steric crowding between the phenyl and cyclopropyl groups which prevents an optimum conformation of any one for maximum conjugation, i.e. coplanarity of the former and a bisecting arrangement of the latter with respect to the double-bond plane.

Turning to the γ -phenyl substituted cyclopropyl acrylic esters we note that the introduction of a terminal phenyl group to the linear chromophore exerts no significant change in the UV absorption. The lack of any extended con-

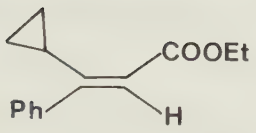
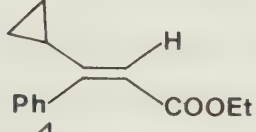
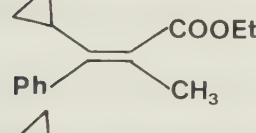
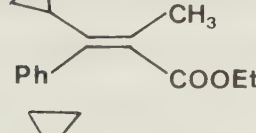
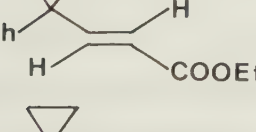
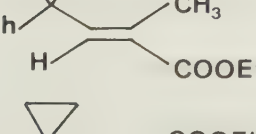
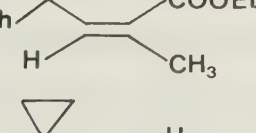
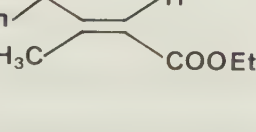
			UV λ_{max} nm	auxochromic effect $\Delta\lambda$
77		E	241	+3 ^{a)} -36 ^{b)}
77		Z	209	-27 ^{a)} -61 ^{b)}
78		E	238	-5 ^{a)} -39 ^{b)}
78		Z	210	-30 ^{a)} -60 ^{b)}
62		E	225	-7 ^{c)}
63		E	226	+2 ^{c)}
63		Z	212	+2 ^{c)}
72		E	235	+4 ^{c)}

Table 1: a) References: the corresponding β -methyl cyclopropylacrylic esters

b) References: the (E)- and (Z)- cinnamic esters

c) References: the corresponding γ -methyl cyclopropylacrylic esters

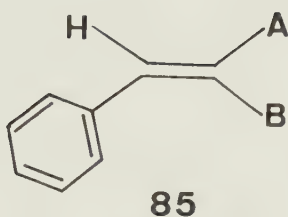
jugation has two reasons: A 1,1-di- π -substituted cyclopropane corresponds to a cross-conjugated situation. Also, one may add that cyclopropanes do not normally transmit π electron conjugation³⁶.

In the NMR, the C_β protons in 62, (E)-63 and (Z)-63 are characterized by a small deshielding effect in comparison to the parent cyclopropyl esters and the C_α protons and methyl groups show, on the other hand, a slight shielding.

The esters were saponified to the acids which are all crystalline. An alternative synthesis of acid 54 in better yield was found in the Knövenagel-Döbner condensation of 61 with malonic acid. Treatment of the acids with methyl lithium gave the corresponding phenylcyclopropylvinyl methyl ketones.

The γ -phenylcyclopropyl vinyl ketone 56 exhibits in the IR spectrum two carbonyl band at 1675 and 1700 cm^{-1} of similar intensity. This double absorption is normally assigned to the s-trans and s-cis conformations, respectively, of aliphatic enones. It is of interest to note that the other ketones of this group, i.e. 67, 74, 81 and 82, show only one single carbonyl band at 1698 cm^{-1} ((E)-74) and at 1665-1685 cm^{-1} ((E)-67, (E)-81, (Z)-82). A possible explanation for this phenomenon is that the acetyl group in the trisubstituted olefins is sterically destabilized in the planar dienoid conformations and thus prevents the s-cis and s-trans forms characterized by two separate bands.

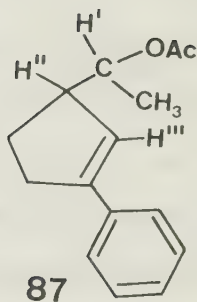
Similar observations and conclusions have been reported e.g. by Currie et al.³⁷ for the system 85. Where $A=\text{COCH}_3$, $\text{CO}_2\phi$, $\text{CONH}\phi$ and $B=\text{H}$ again two carbonyl stretching vibrations appear, whereas in the cases with $B\neq\text{H}$ these two bands coalesce.



The thermal treatment of the aliphatic vinyl ketones resulted in the vinyl cyclopropyl rearrangement to the desired cyclopentenyl methyl ketones. The facility of reaction decreased with increasing substitution of the double bond in the order 66 > 81 > 74 > 57 > 82.

The structure of these acetylcyclopentenenes were assigned on the basis of UV, IR, and NMR data. For the $n \rightarrow \pi^*$ transition in the UV absorption of 68, 69, 75, 83 and 84 see pages 38 and 39. UV maxima around 255 nm of λ 's in the order of 10-20'000 in each case are indicative for a styrene-like chromophore. This assignment is corroborated by the carbonyl stretching frequencies of these ketones at 1710-1718 cm^{-1} which rules out an α, β -conjugated ketone.

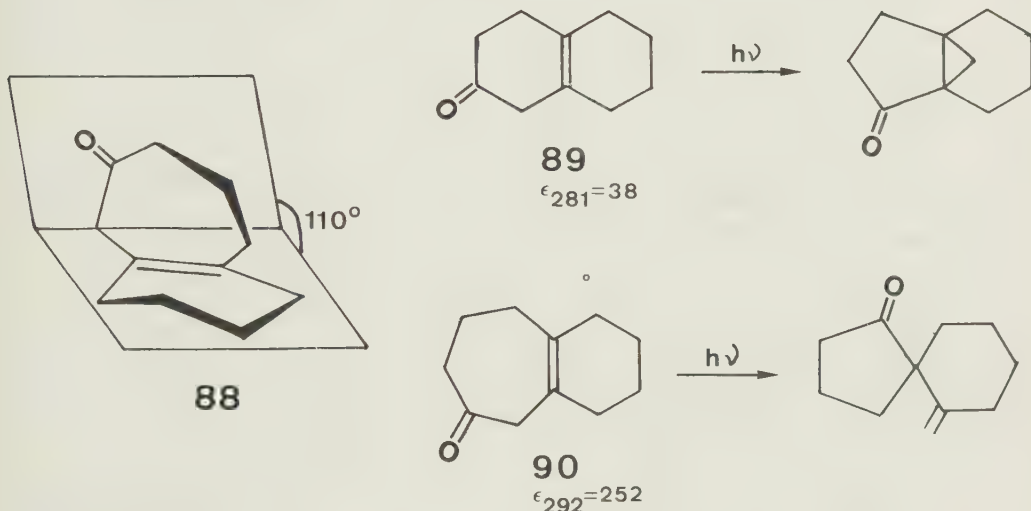
The β, γ -unsaturation was further proven by NMR decoupling experiments with the acetates 87 (a mixture of two diastereoisomers) prepared by sodium borohydride reduction of ketone 68 to the alcohols 86 followed by acetylation. The doublets of CH_3 and of H''' collapse to singlets on irradiation at H' and H'' , respectively. Alternatively, decoupling of CH_3 gives an H' doublet with $J_{\text{H}', \text{H}''} = 9$ and 3 Hz for the two diastereoisomers.



1.4.2 The UV Absorption Spectra of Acetylphenylcyclopentenones

The relative intensities of the $n \rightarrow \pi^*$ transition of these β, γ -unsaturated ketones (Figure 1 p. 38), being a reflexion of their conformations, are involved in directing the singlet state isomerization. On the basis of the discussion in Chapter 1.1 a 1,3-acetyl shift isomerism such as 68 $\rightarrow$ 92 can be expected by analogy for the singlet-excited states of the acetylphenylcyclopentenones; vide infra Chapter 1.4.3. It is well known that homoconjugation, i.e. enhanced $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*/CT$ absorption³⁸ is a necessary requirement for the 1,3-acyl shift in β, γ -unsaturated ketones. When the angle between the two planes formed by the carbonyl group and the double bond is decreased from 180° the π orbitals of $C_{=O}$ and $C_{=C}$ point at one another and thus provide for "through-space" overlap (cf. 88). α -Cleavage is more likely to occur in the latter

conformation since the C_{α} -2p-orbital forming in this process overlaps with the olefinic double bond^{39, 40}. These properties are demonstrated with the examples below (89, 90)^{40, 41}.



In compounds 68 and 69 the homoconjugation is quite pronounced (Table II). No steric hindrance appears to oppose in these molecules the conformation for optimum overlap between the carbonyl group and the styrene double bond. In addition, the electron-releasing effect of the γ -phenyl renders the double bond richer in electrons and causes a more enhanced absorption in the $n \rightarrow \pi^*$ region in comparison with the acetylcyclopentenones lacking phenyl substitution.

One might expect 75 to have an $n \rightarrow \pi^*$ extinction coefficient comparable to that of 68 and 69 since the interacting chromophores are exactly the same. However, from a model it is evident that the phenyl group has to twist out of the double-bond plane owing to steric interaction with the β -methyl group. Such a twist may suffice to explain the observed absorption of 75, i.e. the lowering of both the

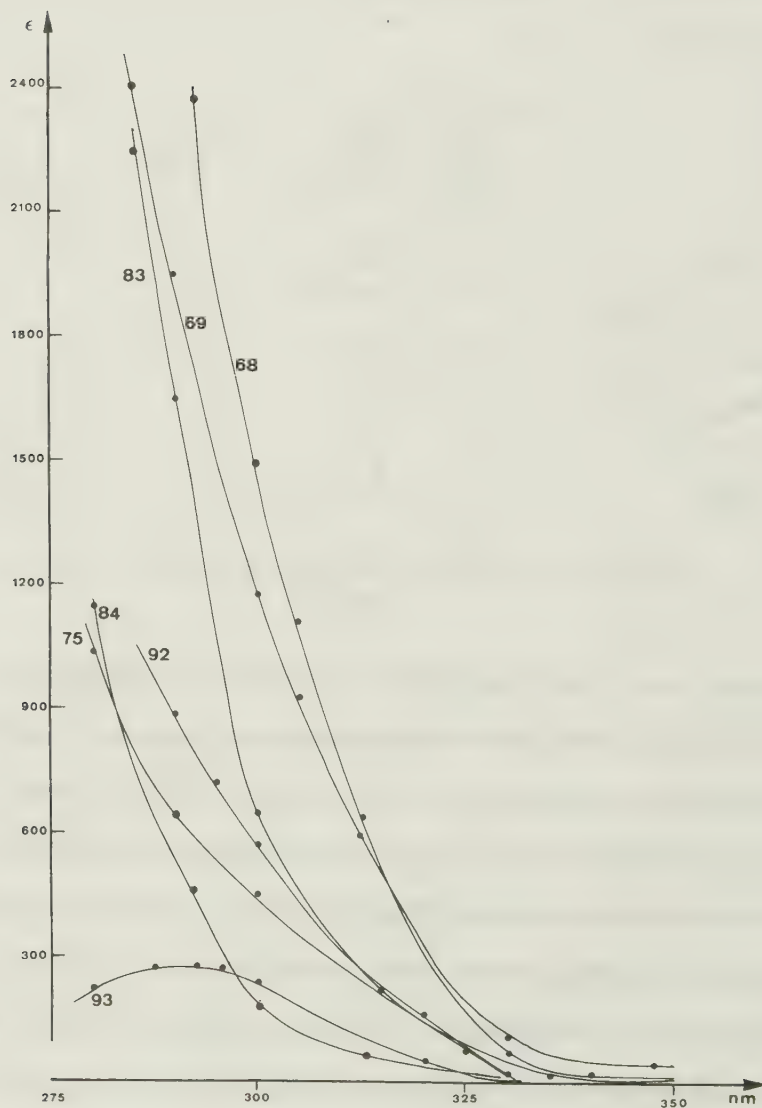
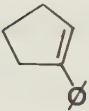
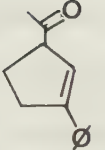
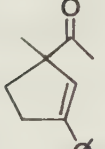
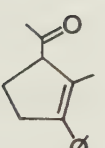
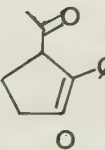
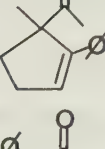
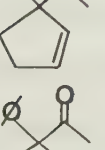
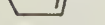


Figure 1: UV Absorption Spectra of Compounds 68, 69, 75, 83, 84, 92 and 93.

Table II

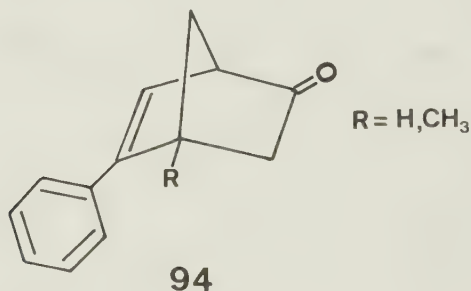
IR and UV Absorption Spectra

Compound	ϵ $n \rightarrow \pi^*$ 313 nm	ϵ $n \rightarrow \pi^*$ 300 nm	ϵ $\pi \rightarrow \pi^*$ max	IR C=O stretching
91 			12600	
68 	630	1500	20000	1718
69 	600	1200	18000	1710
75 	240	455	15000	1710
83 	260	650	10000	1715
84 	83	183	10000	1710
92 	270	590	1400	1712
93 	80	250	290	1710
1 	101			1710

conjugative $\pi \rightarrow \pi^*$ styrene transition and the electron density in the double bond responsible for enhanced homoconjugation.

The UV $n \rightarrow \pi^*$ absorptions of 68, 69 and 75 find an interesting parallel in the phenylbornenone system 94 studied by Cookson⁴¹. The steric requirements for carbonyl and olefin interaction seem to be ideal here, hence $\epsilon_{318} = 6170$.

When $R = \text{CH}_3$, the $n \rightarrow \pi^*$ intensity is lowered to $\epsilon_{315} = 2560$. The explanation offered for this effect is the same as advanced above for 73: repulsion between phenyl and bridgehead methyl decreases the styrene conjugation (hence the electron density in the double bond) by out-of-plane twisting.



The absorption spectra of compound 83 also shows a smaller homoconjugation when compared to 68 and 69. This may be due at least in part to the nonlinear arrangement of ketone, double bond and phenyl. $\text{C}=\text{O}$ orbital overlap with the β -carbon involves now the π -system at the central $\text{C}=\text{C}$ position rather than at the terminal carbon of the styrene. The difference in electron density at these styrene $\text{C}=\text{C}$ positions could possibly account for the varied homoconjugation in the two overlap situations. In compound 84 this decrease in ϵ is even more pronounced. In accordance with the steric arguments given above the additional α -methyl should effect a phenyl twist and account for the appreciable further

loss in conjugation.

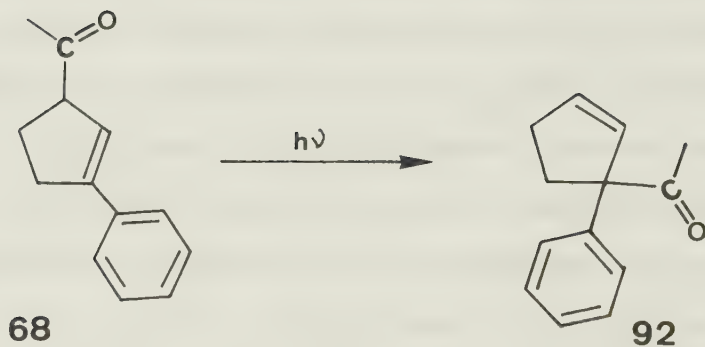
Turning to the $\pi \rightarrow \pi^*$ data one notes that the proposed styrene twist in 75 and 84 has no significant influence on the absorption as may be expected for a relatively small out-of-plane conformation⁴² (cf. the data for 69/75 and 83/84).

Furthermore, we see a reasonably good direct correlation of the transition probabilities of the two bands in accordance with the phenomenon of homoconjugation³⁸.

Comparison of the ultraviolet absorption of 92 and 93 shows a distinct decrease in ($n \rightarrow \pi^*$) in 93, though the latter is still a β, γ -unsaturated ketone. However, homoconjugation with a phenyl group is less favorable than with a double bond since the electron density is appreciably lower in the former π -system. Alternatively, it appears remarkable - and at present difficult to rationalize - that compound 92 with both phenyl and double bond in " β -positions" exhibits a greater homoconjugation than the purely olefinic ketone 1.

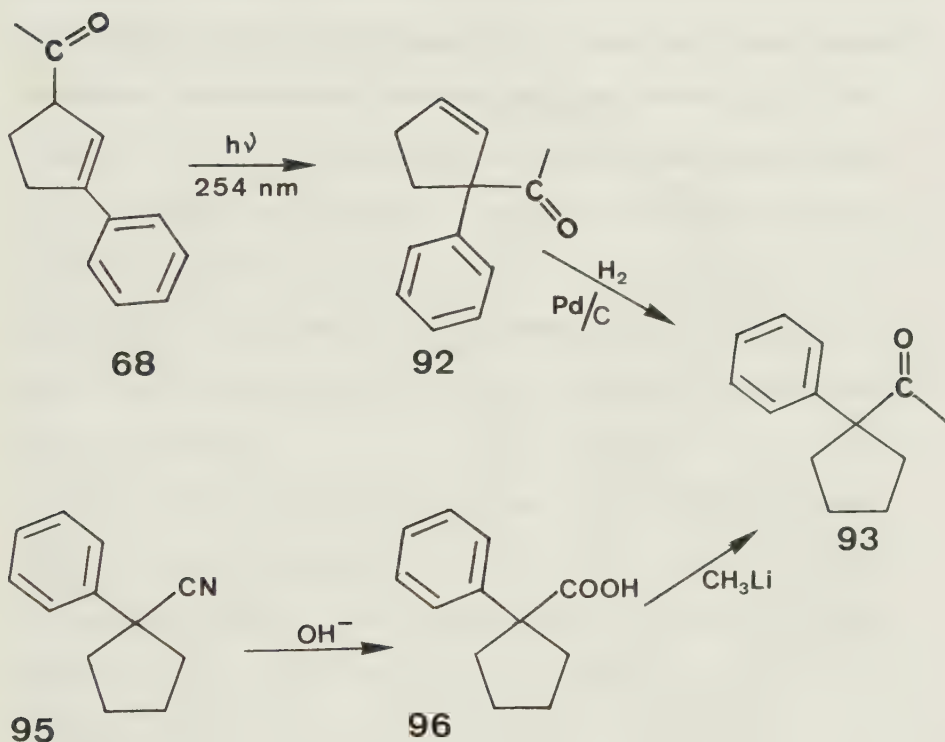
1.4.3 Direct Irradiation of 1-Phenyl-3-acetyl-1-cyclopentene (68)

Direct photolysis of 68 at room temperature and > 300 nm in benzene resulted in the formation of product 92. After complete conversion of starting material the reaction mixture had become brownish and some material of apparently higher molecular weight had been deposited on the wall. In the solution, however, no other product but 92 was detectable by VPC and NMR analysis.



Preparative irradiations were most conveniently carried out at 254 nm in ether. After all starting material had disappeared, isolation by silica gel column chromatography gave 92 in 52% yield. The quantum yields of consumption and of product formation were 0.26 and 0.085, respectively (cf. Table III). The structure of 92 was established by catalytic hydrogenation to 93 which was also prepared by acid-catalyzed hydrolysis of 1-cyano-1-phenylcyclopentane (95)²⁹, followed by treatment of the acid 96 with methyl lithium (Chart 4).

Chart 4

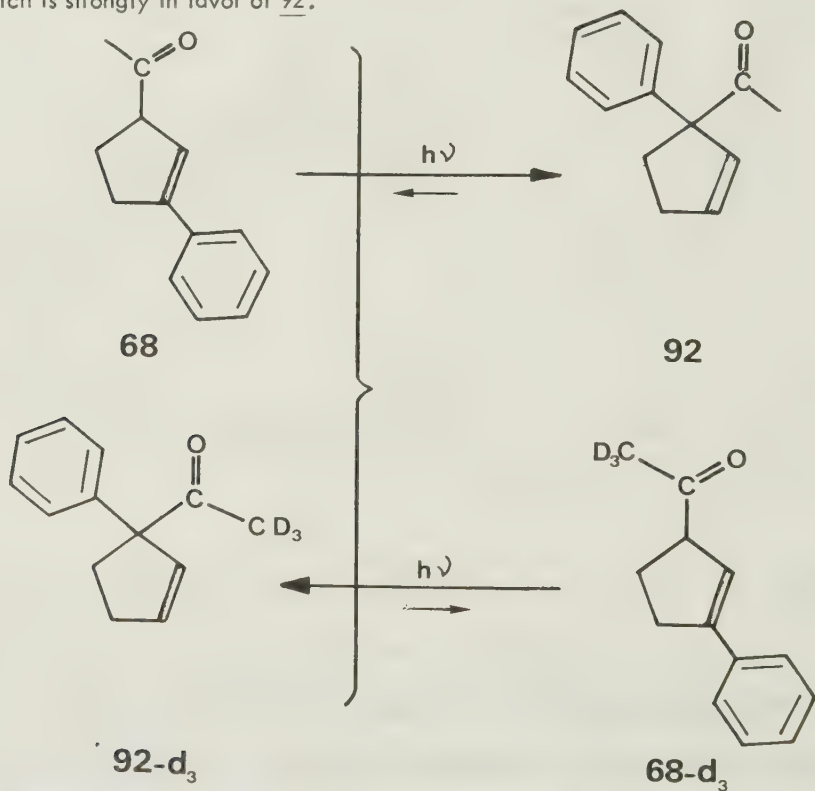


The NMR spectra of **92** in $CDCl_3$ and in C_6D_6 show a singlet at δ 6.10 and a complex multiplet around δ 5.80, respectively, for the two olefinic protons.

Upon separate irradiation of **92** under the conditions of its formation no isomerization back to **68** could be observed by VPC. The limit for detection of **68** in this experiment is estimated to be ca. 5%, i.e. an undetected photostationary equilibrium between **68** and **92** would have to be in the order of $> 20:1$.

The irradiation of a 1:1 mixture of **68** and deuterium-labelled ketone **92-d₃** at > 300 nm in benzene was designed to uncover the existence of such a photo-

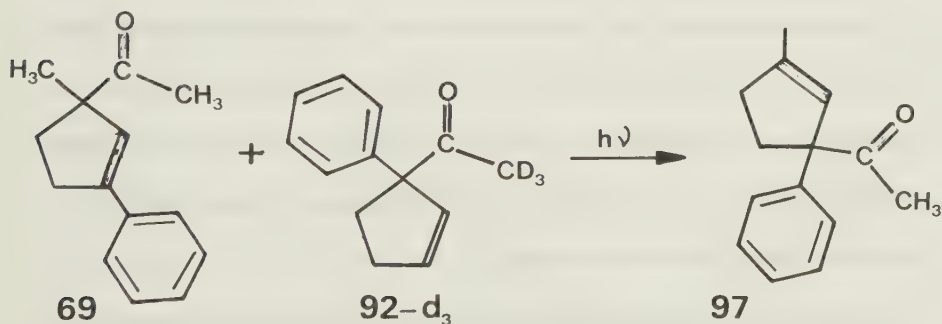
stationary equilibrium. After 60% disappearance of 68, the remaining ketone was admixed with ca. 10% 68-d₃ (m/e = 189/186, 143, 46/43). In the absence of intermolecular exchange of acetyl (see below) this result proves the occurrence of the 1,3-acetyl shift 92-d₃ → 68-d₃ and hence, a photostationary equilibrium which is strongly in favor of 92.



The intramolecular nature of the 1,3-acetyl shift was established with another experiment involving a two-component mixture, which now required a label on both the acetyl and the phenylcyclopentene moieties, either combined in one or distributed among both starting components. Since preliminary attempts to prepare a tetradeuteriated ketone by base-catalyzed H/D exchange in 68 failed, the photolysis of 69 + 92-d₃ was envisaged. In fact, the result of the direct

irradiation of 69 proved entirely analogous to that of 68: again a clean isomerization of 69 to product 97 was observed (concomitant with formation of insoluble material). The structure of this compound was assigned on the basis of its NMR data (a doublet at δ 1.80, $J=1$ Hz, for the olefinic methyl group and a multiplet at δ 5.60 for the olefinic proton) and of an MS fragmentation pattern which closely resembles that of the desmethyl analog 92 (m/e = 186, 143, 128, 115, 91 and 43 for 92, and m/e = 200, 157, 142, 129, 91 and 43 for 97). The 1,3-acetyl shift established above for 92-d₃ rendered this ketone a conveniently accessible second component with the potential capacity as a source of acetyl and phenylcyclopentenyl radicals in the mixed photolysis.

Irradiation of a 1:1 mixture of 69 + 92-d₃ in benzene at > 300 nm, isolation by VPC and MS analysis of 92-d₃ and 97 after ca. 80% conversion of 69 indicated total lack of d₃ scrambling, i.e., 92-d₃ and 97 had retained the initial isotope distribution.



The trend in the direct photolysis of many β, γ -unsaturated ketones is formation of a photostationary equilibrium favoring the component with the least α -substitution. Engel and Ziffer⁸ have rationalized this observation with the plausible suggestion that the rate of α -cleavage increases with α -substitution. The reverse

result with the γ -phenyl-substituted acetylcyclopentene 68 may not necessarily constitute a true exception to this rule, but it may merely reflect overcompensation due to the difference in extinction coefficients ($\epsilon \frac{68}{300} = 1500$ and $\epsilon \frac{92}{300} = 590$). Of course, other factors may additionally attribute to the net result. When we consider the equilibrium $4 \rightleftharpoons 5$ we note that 5 is favored over 4 in a 3:1 ratio, thus obeying the above substitution rule. If one takes this product pair as the best available reference to 68 and 92 and takes the absorption difference in the latter into account, one would expect an approximately 1:1 ratio for 68 $\rightleftharpoons$ 92 in the absence of any other controlling factors. In order to rationalize the much greater preference for 68 $\rightarrow$ 92, an electronic factor may be invoked which is introduced by the extension of the double bond (in 4/5) to a styrene system (in 68/92)^{42, 43}. Thus, regarding the less likely bridging mechanism (cf. 7), one may argue that the electron density in the styrenyl-type allyl radical is greatest at the carbon carrying the phenyl group rather than at the terminal carbon (see 6). Bonding of acetyl to the former carbon should therefore be preferred. This argument does not prejudice a mechanistic distinction between a concerted pathway and a stepwise reaction via a radical pair similar to 6. This latter mechanism, while excluded for the acetylcyclopentenenes lacking phenyl substitution, still remains a possibility for the system 68 $\rightleftharpoons$ 92.

The second, and chronologically primary mechanistic aspect of the reaction 68 $\rightleftharpoons$ 92 which has not been resolved as yet, concerns the multiplicity of the reactive state. The situation is the same in this point as with most other β, γ -unsaturated ketones. It will be shown in Chapter 1.4.4 that triplet sensitization of 68 leads to ODPM rearrangement at the expense of the 1,3-shift observed

upon direct excitation. This rigorously excludes the lowest-lying triplet state of 68 for the acetyl shift reaction and leaves a higher-lying triplet state or the n, π^* singlet state as the remaining possible species.

A final and equally unresolved problem related to the direct irradiation of 68 concerns the observation of strong phosphorescence at 77K in EPA. Yet, no detectable amount of triplet photoproduct was found. Even at -100°C and $> 300\text{ nm}$ in ether after 25 hours, neither singlet nor triplet photoproducts were in fact detected although the starting material had gradually decreased. The quantum yield of phosphorescence of 68 is 0.05. Its origin and importance related to the triplet reaction will be discussed in Chapter 1.4.4. Phosphorescence upon excitation at 258 nm at 77K in EPA is also observed with 92 and irradiation at 254 nm in ether effects again no visible change, and in particular no formation of 1-phenyl-5-acetylbicyclo[2,1,0]pentane (98). The point of interest in connection with the 1,3-acetyl shift is that the competition between migration (upper-excited state reactivity) and the pathway(s) to the lowest-lying triplet turns in greater favor for the former reaction at higher temperature in liquid solution. There are several possible reasons which can be considered responsible for this behavior: 1) The acetyl migration $\underline{68} \rightleftharpoons \underline{92}$ may become more efficient at higher temperature and may override the transformation of the upper excited state (responsible for migration) into the lowest-lying triplet. This would imply that the migration has to overcome an activation barrier, a possibility which is consonant with any of the reaction mechanisms considered. (One may, in fact, argue that contrary to a still widespread opinion a photochemical reaction devoid of any thermal activation energy requirement is an exception rather than a rule.

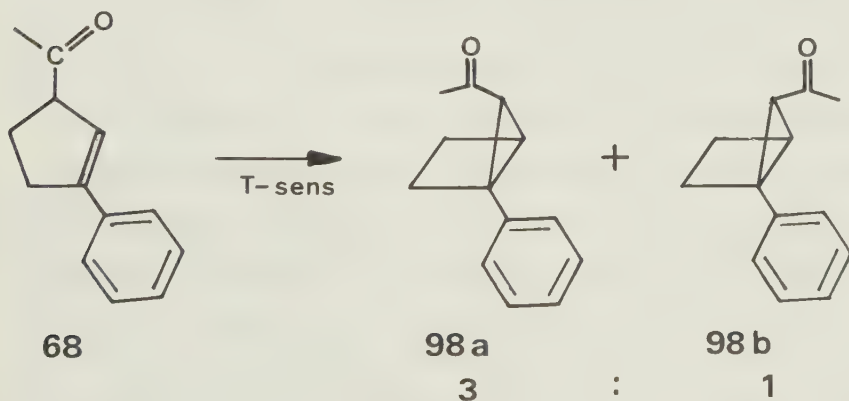
The very frequent apparent lack of an activation energy at room temperature in photoreactions reflects merely the existence of relatively shallow energy minima and maxima on the excited-state surface when compared to the energetic topology of the ground state.) 2) Another factor, and possibly in addition to the above point, is much more complicated to assess. Ketone 68 in the ground state as well as in the excited states can in principle exist in different conformations, due to conformational equilibria of the cyclopentene moiety (placing the acetyl group in pseudo equatorial and axial positions) and rotational isomerism of the acetyl side chain. The population of these different conformers at different temperatures will certainly vary in ways which are presently not known, and the reactivity and physical properties of each conformer distribution must necessarily differ as well.

It seems appropriate here to shortly consider a possible experimental approach to solve this rather complex problem, although it was beyond the scope of this work. The ketone, preferably 69, should be resolved into its enantiomers. An extensive correlation of the conformer population, as analysable by means of a CD temperature gradient study, of phosphorescence and of reactivities in the entire temperature range spanning from 77K to room temperature may lead to a sufficiently comprehensive insight and may eventually give the required answers. A similar approach, though less far-reaching, has been carried out successfully in the investigation of the photodecarbonylation of aldehydes similar to compounds 1⁴⁴.

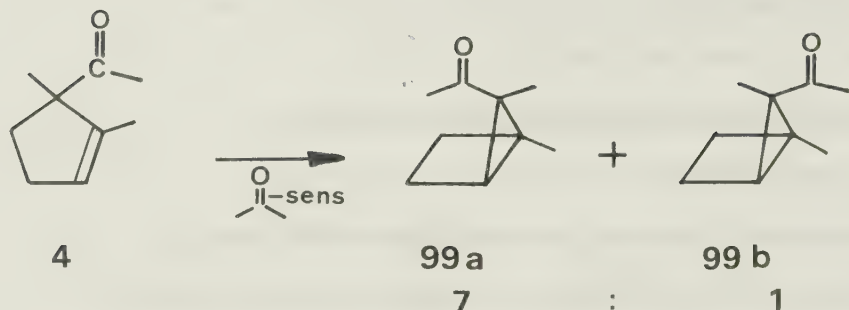
1.4.4. Triplet Sensitization of 1-Phenyl-3-acetyl-1-cyclopentene

1.4.4.1. Preparative Experiments and Product Analysis

Irradiation at > 340 nm of a nitrogen-purged benzene solution of 68 at room temperature with a sufficient amount of benzophenone ($E_T = 68$ kcal/mol) to absorb $> 95\%$ of the incident light, gave rise to the endo- and exo- acetyl-bicyclopentanes 98a and 98b. The two stereoisomers were inseparable by chromatographic methods, but their ratio of ca. 3 (98a) : 1 (98b) could be estimated by NMR integration of the methyl singlets. No other photoproduct was detectable by VPC or NMR.



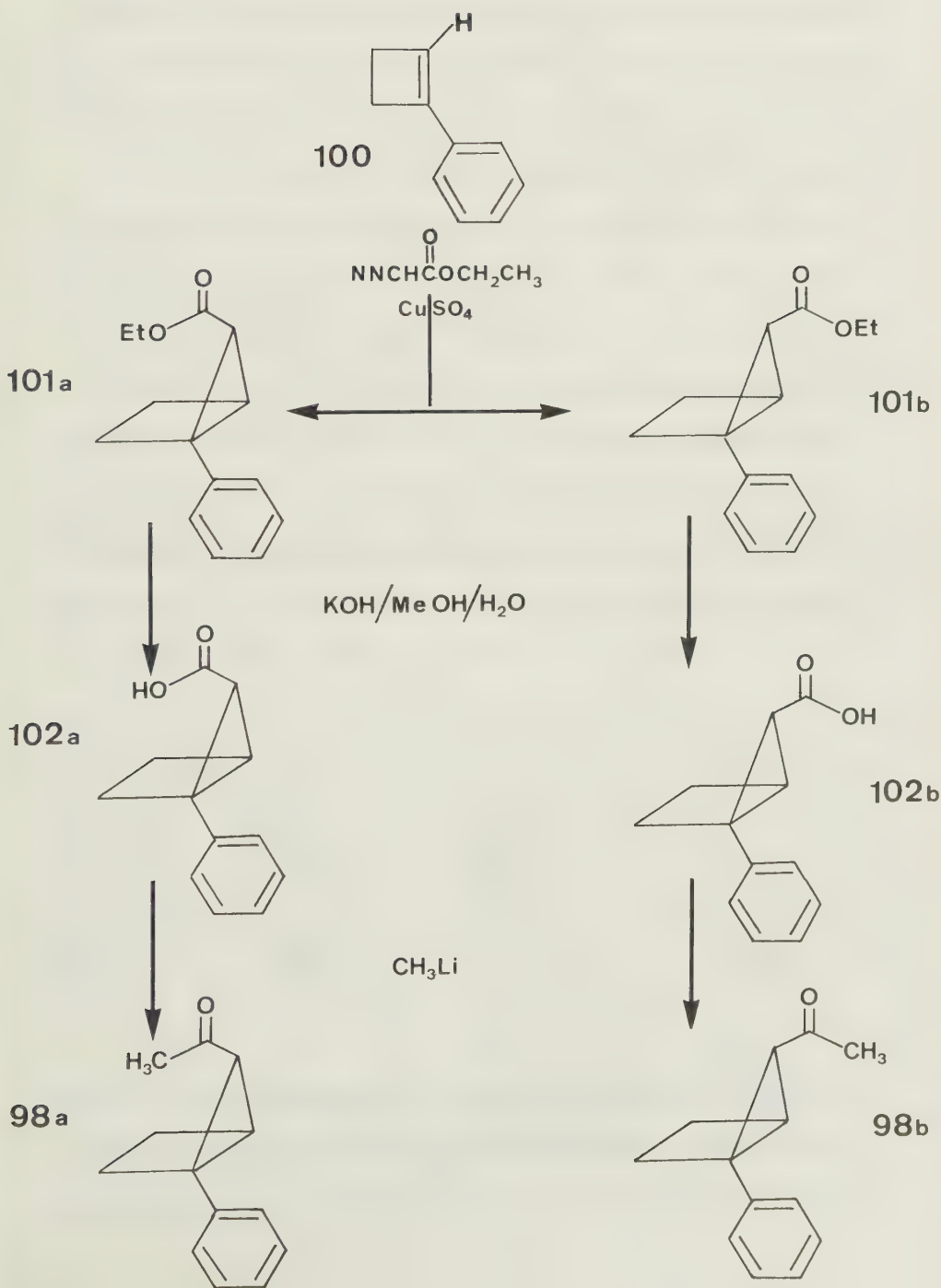
This result is quite similar to the well-known triplet ODPM rearrangement of double-bond constrained β, γ -unsaturated ketones^{1, 2, 3} and especially to that of the acetylcyclopentenones of type 1⁵, which also lead to the endo- and exo-isomers with a preference for the endo configuration (cf. 4 $\rightarrow$ 99a+b).



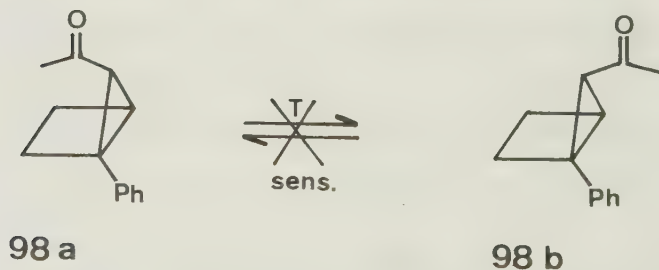
The constitution of the two products 98a and 98b was established by their separate synthesis from 1-phenylcycobutene (100)⁴⁵ (Chart 5). CuSO_4 -catalyzed reaction⁴⁶ of ethyl diazoacetate with 100 gave a 2:3 mixture of the endo- and exo-esters 101a and 101b in a 63% total yield. The carbonyl stretching frequencies were 1735 and 1730 cm^{-1} , respectively. After separation by silical gel column chromatography they were hydrolyzed quantitatively to the corresponding crystalline acids 102a,b with KOH in aqueous methanol and then converted to the methyl ketones 98a,b with methyl lithium in 48% and 67% yield for the exo- and endo-isomer, respectively. The carbonyl frequencies are 1705 and 1710 cm^{-1} , respectively. The UV spectra are quite similar. The absorption intensities indicate some transmission of conjugation by the cyclopropane between ketone and phenyl group, in contrast to what is generally observed in similar but acyclic arrangements³⁶.

Strong evidence for the endo/exo configurational assignment was provided by the NMR data of the two isomers 98. A shielding effect by the cis-oriented phenyl group in the exo-compound 98b on the acetyl protons shifts the methyl singlet to $\delta\ 1.80$ (cf. $\delta\ 2.18$ for 98a). Furthermore, a selective deshielding effect by the shift reagent $\text{Eu}(\text{FOD})_3$ on the aromatic ortho-protons was observed.

Chart 5



Confirmation of the above configurational assignment came forth in an X-ray diffraction analysis of the acid 102b, the synthetic precursor of the exo-ketone 98b, by Bernardinelli et al.⁴⁷; see Figure 2 for the full molecular structure. Under the irradiation conditions of their formation the acetylbicyclopentanes 98a and 98b did not interconvert and remained unchanged. Substitution of acetophenone and acetone as sensitizers for benzophenone did not effect interconversion of 98a and 98b either, but both starting ketones were slowly consumed without appearance of other photoproducts in the VPC and NMR. Possibly the triplet energy of benzophenone is too low for sensitization, and the triplet-excited ketones 98 when sensitized by the higher-energy donors, decompose to VPC- and NMR-undetected material of higher molecular weight rather than stereomutate. The result of these experiments proves that the 3:1 composition of 98a+b represents the primary ratio formed photolytically.



The failure of 98a and 98b to interconvert photochemically parallels the previous similar finding by Gonzenbach⁵ and Grosclaude⁴⁸ with 99a,b, and it contrasts the observation by Dauben⁴⁹ that trans-1-acetyl-2-methylcyclopropane (103) is

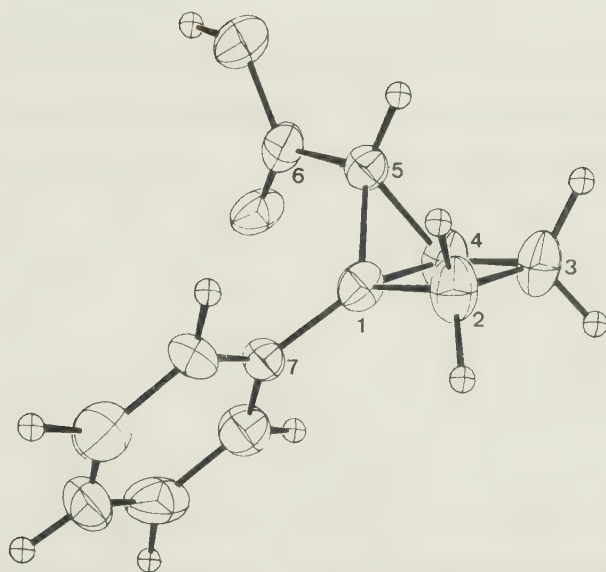
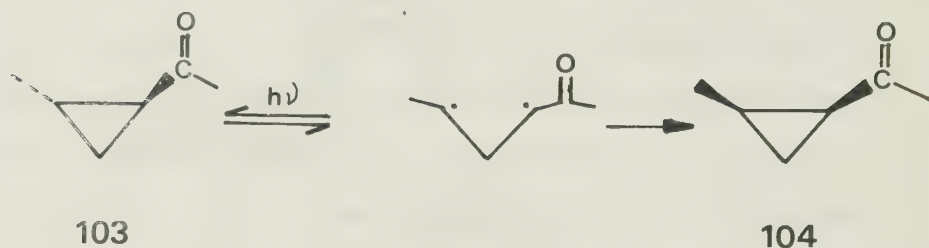


Figure 2: X-ray structure of exo-1-phenylbicyclo(2,1,0)pentane-5-carboxylic acid.

The following crystallographic data were determined for the exo-acid 102b: Monoclinic, space group $P2_1/c$, $a = 6.121(3)$, $b = 24.567(8)$, $c = 7.159(3)\text{\AA}$, $\beta = 111.83(4)^\circ$; $V = 999.34\text{\AA}^3$; $Z = 4$; $F(000) = 400$; $D_m = 1.267$, $D_x = 1.251\text{ g/cm}^3$; $\mu = 0.908\text{ cm}^{-1}$.

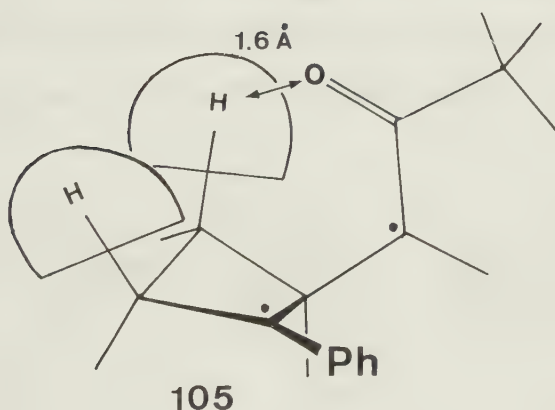
Bond distances ($\text{\AA}$).		Bond angles ($^\circ$).	
C(1)—C(2)	1.554(9)	C(2)—C(1)—C(4)	89.5
C(1)—C(4)	1.528(6)	C(2)—C(1)—C(5)	106.6
C(1)—C(5)	1.549(7)	C(2)—C(1)—C(7)	123.0
C(1)—C(7)	1.472(8)	C(4)—C(1)—C(5)	59.1
C(2)—C(3)	1.573(7)	C(4)—C(1)—C(7)	134.5
C(3)—C(4)	1.528(9)	C(5)—C(1)—C(7)	125.5
C(4)—C(5)	1.517(7)	C(1)—C(2)—C(3)	89.5
C(5)—C(6)	1.481(9)	C(2)—C(3)—C(4)	88.8
		C(1)—C(4)—C(5)	61.1
		C(3)—C(4)—C(1)	92.1
		C(3)—C(4)—C(5)	109.0
		C(1)—C(5)—C(6)	115.4
		C(4)—C(5)—C(1)	59.8
		C(4)—C(5)—C(6)	115.1

readily converted to the *cis*-isomer (104) by direct irradiation. It is possible that



the photostability of ketones 98 is due to a thermally reversible " π^* -assisted"⁵⁰ cleavage of the three-membered ring. Conditional to such a photochemical energy dissipation would be that in the 1,3-diradical intermediate(s) of type 105 rotation around the remaining of the former external cyclopropane bonds prior to reclosure be prevented. Inspection of molecular models of such intermediates reveals in fact strong steric inhibition to rotation. Thus, 105 represents the product of the most likely bond cleavage between the acetyl and phenyl substituents in the conformation with the largest minimum distance between endo-methylene hydrogen and radical side chain which has to be overcome in a full rotation. This nonbonding interatomic distance measures ca. 1,6 Å for O--H_{endo-methylene} and may impose a sufficient barrier to rotation at room temperature. Any other conformation throughout the rotation includes even shorter nonbonding distances if it is assumed that the α -ketoradical and benzyradical partial structures retain planar arrangements (greatest stabilization through maximum orbital overlap) during the entire process. E.g., a rotation in which the α -ketoradical hydrogen passes by the nearest endo-methylene hydrogen would include simultaneously an even more prohibitive steric interaction than

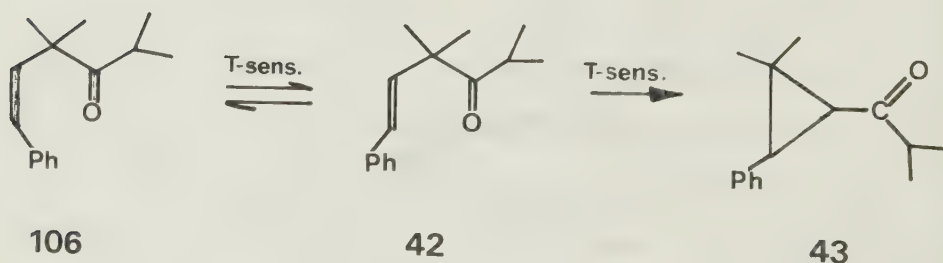
the above-mentioned between the oxygen and the phenyl ortho-hydrogen. A similar argument was discussed by Grosclaude⁴⁸ for the case of 99a $\rightleftharpoons$ 99b in which the largest minimum distance is ca. 1,6 Å for O--H and 1,4 Å for H--H.



Sensitization of 68 was also carried out with a number of other triplet donors with 0—0 triplet energies ranging from ca. 56 to 80 kcal/mol. Acetone ($E_T \approx 80$ kcal/mol) sensitization at > 300 nm failed to give any detectable photoproduct. Starting material had completely disappeared, however, after ca. 15 hours of irradiation. Examination of the photoreaction mixture already after short exposure to light showed only degradation of starting material. This could mean either that photoproducts 98 are never formed during the photolysis, or that they are - perhaps more likely - rapidly destroyed, since the acetylbicyclopentanes proved unstable under these conditions.

Sensitization with acetophenone at > 300 nm and with thioxanthone and Michler ketone at > 340 nm resulted in the same clean appearance of endo- and exo-acetylbicyclopentanes (98). The product composition was the same as with benzophenone. When α - and β -acetonaftone were used as triplet donors, no reaction occurred.

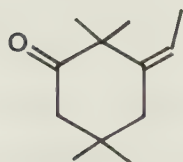
These results can be related to the interesting but only qualitative finding by Dauben⁴ with the analogous ketone 42, which contains an acyclic styrene moiety.



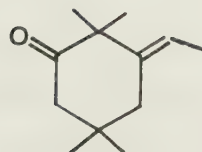
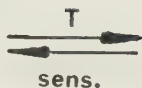
Cyclopropylketone 43 was formed when acetophenone, benzophenone and α -acetonaftone were used as sensitizers, which places the reactive triplet of 42 energetically definitely below the estimated range of 79 - 81 kcal/mol for the n, π^* triplet⁵¹.

This case belongs to one of the few examples of ODPM rearrangements which occur, although inefficiently, in rotationally flexible systems. The triplet reaction of β, γ -unsaturated ketones possessing acyclic double bonds rather favors cis-trans isomerization than ODPM rearrangement owing to the "free rotor" effect. An example has been presented by Hancock¹⁶ (107 $\rightarrow$ 108), which contrasts the triplet reaction of a similar but conformationally constrained

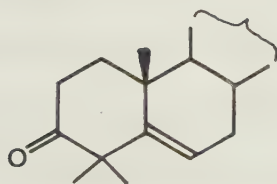
system⁵² (109 → 110).



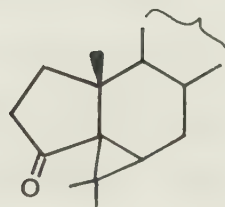
107



108

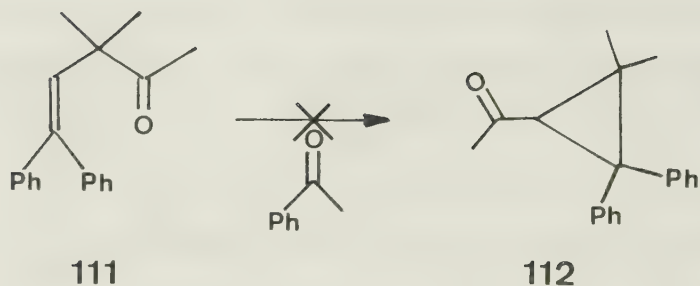


109

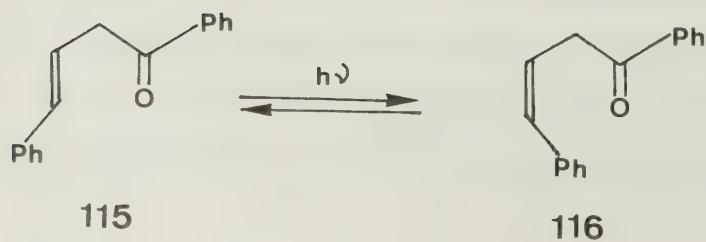
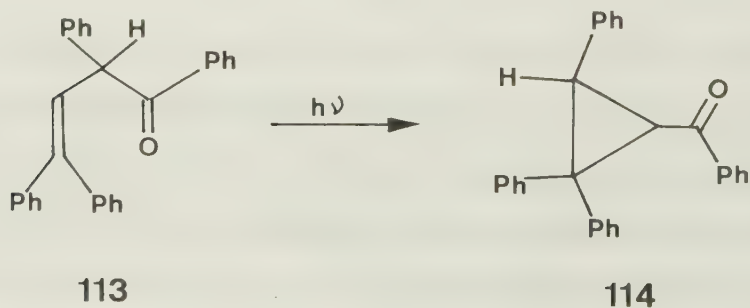


110

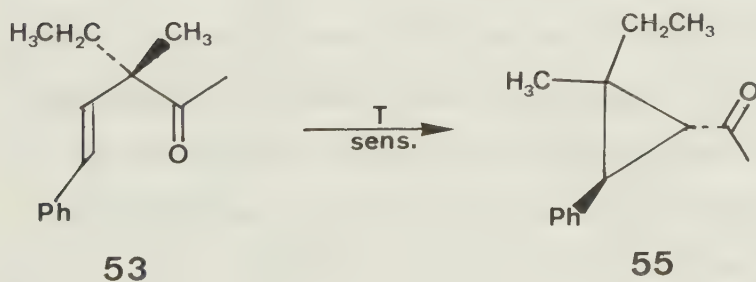
The finding by Dauben may be put in relation to similar systems with extended olefinic chromophores. Pratt⁵³ reported that acetophenone sensitization of 111 did not give any cyclopropyl ketone, which is in marked contrast to the result of 42 as the lowest triplet state is also most likely of π, π^* character owing to the diphenyl ethylene moiety.



Parallels may also be drawn to the work of Tenney⁵⁴ (113 → 114) and that of Cowan and Baum⁵⁵ (115 → 116). In the former case 7% of cyclopropyl ketone were obtained, but in the latter exclusively cis-trans isomerization was observed, which could only partially be quenched by triplet quenchers.



One may conclude that the 1,2-shift will occur when it can compete efficiently with the free rotor energy dissipation, i.e., when a sufficiently large orbital mixing in the triplet state is present, which is also reflected in the $n \rightarrow \pi^*$ enhancement. Thus, in compounds with enhanced $n \rightarrow \pi^*$ absorption the ODPM rearrangement can compete more effectively with other nonradiative pathways. This would rationalize the ODPM rearrangement of 42 ($\epsilon_{293}=376$) and of 53 ($\epsilon_{290}=350$), and the free rotor efficiency in 111 ($\epsilon_{295}=120$). In order to explain the difference in behaviour of 113 and 115, one would then have to postulate in line with the above argument that the triplet of 113 exhibits greater $n, \pi^*/\pi, \pi^*$ orbital mixing than the triplet of 115. The literature does not give any data relevant to this point.



1.4.4.2 Identification of the Reactive Triplet State of 68

From the sensitization experiments with 1-phenyl-3-acetyl-1-cyclopentene (68) we expected its lowest-lying triplet state to correspond closely to the relatively low-lying $^3(\pi, \pi^*)$ -state of styrene with little perturbation by the carbonyl group. Moreover, twisting around the double bond is limited in the five-membered ring of 68 and its parent styrene, 1-phenylcyclopentene (91). Radiationless triplet deactivation should therefore be restrained in favor of emission at low temperature, and the lowest triplet energy of the two compounds should approximate the spectroscopic $S_0 \rightarrow T_1$ transition energy measured for styrene by absorption under high pressure of oxygen (61.7 kcal/mol)⁵⁶. These expectations were met by phosphorescence emission spectroscopy and sensitization quantum yields. Both ketone 68 and 1-phenylcyclopentene (91) exhibited in ether/isopentane/ethanol 5:5:2 and in 3-methylpentane at 77K phosphorescences ($\Phi_p = 0.05 \pm 5\%$, $\tau_p = 120$ ms, and $\Phi_p = 0.003 \pm 50\%$, $\tau_p = 625$ ms, respectively) which are superimposable in spectral shape and energy (0-0 band at 483 nm = 59 kcal/mol). The excitation spectra were in good agreement with the corresponding absorption spectra (see Figure 3).

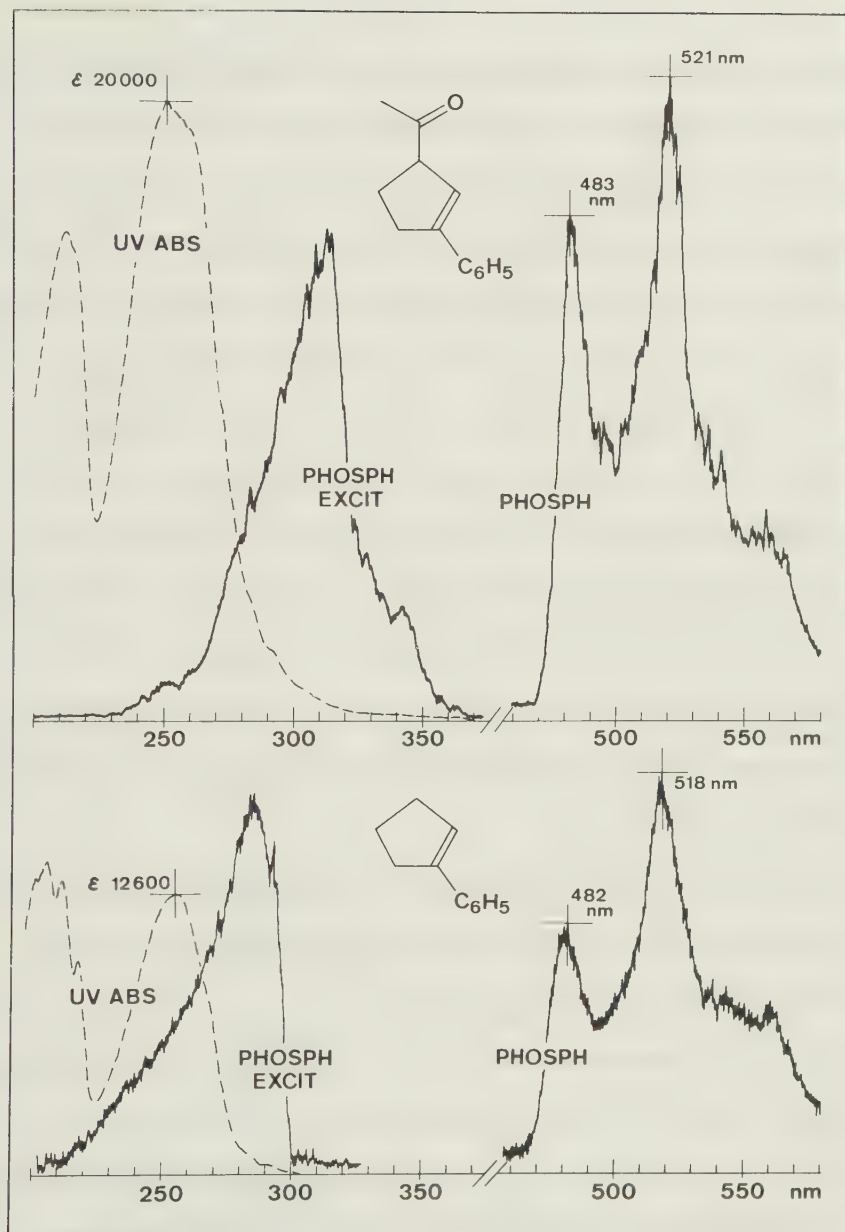


Figure 3: Absorption, phosphorescence, and phosphorescence excitation spectra of 1-phenyl-3-acetyl-1-cyclopentene (68), and 1-phenylcyclopentene (91)

The phosphorescence quantum yields of 68 and 91 differ by a factor of ca. 10, which corresponds exactly to the $S \rightarrow T$ intersystem crossing quantum yield in 91⁵⁷. It is interesting to speculate that this would indicate a Φ_{isc} of ca. 1 for 68, if the two lowest-lying triplets are as similar as their emission indicates. A priori, such would be acceptable in view of the intermediacy of the keto group in the excitation process (ketones tend to have relatively high Φ_{isc} which approach unity in conjugated ketones). This consideration is of course quite crude, but it lets us reiterate the observation that 68 phosphoresces, hence $S \rightarrow T$ intersystem-crosses at low temperature in a solid matrix and yet does not show reaction from T_1 at room temperature in solution. Here again one could arrive at a unified picture, in accordance with present literature proposals^{11, 12}, that intersystem crossing in many β, γ -enones is efficient but populates the T_2 state, and that reaction (the 1,3-shift) from this state prevails when provided by sufficient thermal activation.

The exact similarities in spectral shape and T_{0-0} band energy of 68 and 91 led us to the conclusions that these two compounds have the same lowest triplet configuration corresponding to a π, π^* state.

Quantum yields for consumption of starting material, Φ_{-68} , and product formation, Φ_{98} , were measured at room temperature in liquid solutions and are listed in Table III. The endo-exo product ratio in runs 2-5 were determined by NMR after each irradiation experiment, i.e. at highest conversion, and it was found constant (3:1) in all cases. The quantum yields remained quite similar with the first four sensitizers and then dropped to zero for product formation with α - and β -acetophnone (runs 6 and 7). Complete inefficiency of sensitization, i.e. the sharp

Table III. The Rearrangement of 68 on Direct Irradiation and Triplet Sensitization:
Yields of Consumption ($\Phi_{\underline{68}}$) and Product Formation ($\Phi_{\underline{98}}$ and $\Phi_{\underline{92}}$)

Run	Con- centra- tion of <u>68</u>	Sensi- tizer (E_T , kcal/mol)	Exci- tation (nm)	Con- ver- sion %	Quantum Yields		
					$\Phi_{\underline{68}}$	$\Phi_{\underline{98}}$	$\Phi_{\underline{92}}$
1	0.10M	-	313	12-43	0.26	-	0.085
2	0.10M	Aceto- phenone, neat (73.6)	313	9-45	0.085	0.020	-
3	0.10M	0.10M Benzo- phenone (68.5)	366	29-52	0.098	0.035	-
4	0.11M	0.01M Thio- xanthone (65.5)	366	7-30	0.084	0.035	-
5	0.12M	0.01M Michler's Ketone (61.0)	366	17-46	0.083	0.047	-
6	0.12M	0.43M β - aceto- naphthone (59.3)	366	2-13	0.03	-	-
7	0.10M	0.22M α - aceto- naphthone (56.4)	366	4-11	0.016	-	-

drop in Φ_{68} begins at $E_T^{\text{sens}} = 59$ kcal/mol which is about equal to that of the acceptor. No efficient exothermic transfer is possible anymore at this point.

It should be noticed that all triplet energy data given here are taken from phosphorescence spectra measured at low temperature in rigid glass. In fluid solution at room temperature these energy values tend to be lower by a few kcal/mol⁵⁸.

It is possible, therefore, that the triplet energy of 68 is slightly higher than that of β -acetonaphthone under the conditions of sensitized irradiation.

We conclude from the quantum yields of sensitization in combination with the phosphorescence results of 1-phenyl-3-acetyl-1-cyclopentene (68) and 1-phenylcyclopentene (91) that the lowest-lying styrene-type π, π^* triplet of 68 is the excited state responsible for the ODPM rearrangement to endo- and exo-1-phenyl-5-acetylbicyclo[2.1.0]pentane (98a,b).

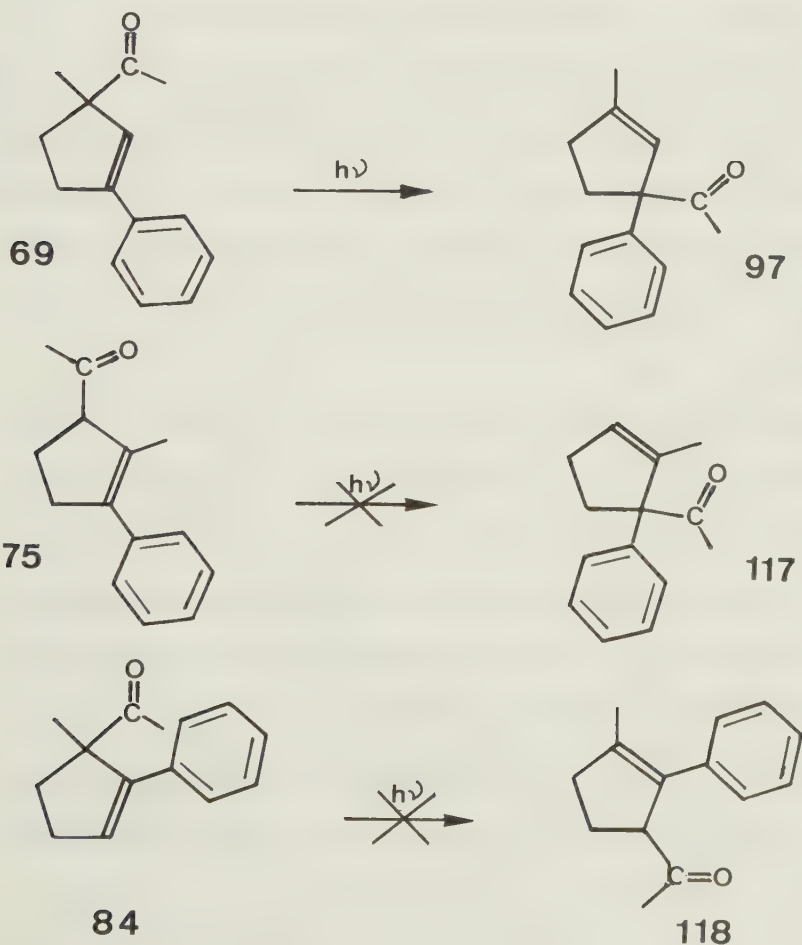
Regardless of the failure of the α - and β -acetonaphthones to sensitize the ODPM rearrangement to 98, these compounds persist to destroy 68 although less efficiently than do the sensitizers of higher triplet energy. This behaviour is reminiscent of similar observations by Engel⁵¹ with several other β, γ -unsaturated ketones.

This author suggests that interaction of ground-state ketone with aromatic ketone triplets can give rise to an excited complex which may lead to reaction of the sensitizer with β, γ -unsaturated ketones.

Since the quantum yields of product formation remained similar with decreasing sensitizer triplet energy and suddenly dropped to zero around 59 kcal/mol, one may conclude that exciplex formation is not the mode of transfer responsible for the sensitized triplet ODPM reaction of 68, but rather the diffusion-controlled exchange mechanism as treated by Dexter⁵⁹.

1.4.5. Preliminary Photolyses of Other Acetylphenylcyclopentenes

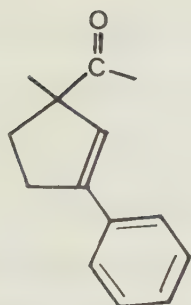
Upon direct irradiation of 69, 75 and 84 under the conditions used for 68, only 69 reacted to give the expected 1,3-acyl shift product 97. 75 and 84 showed no such rearrangement even after several days of irradiation and only slow disappearance of starting material.



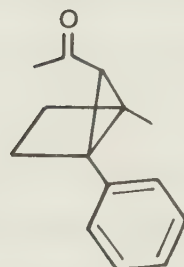
From a comparison of the UV data (cf. page 39) it seems clear that the homoconjugation in 75 and 84 is less pronounced than in 68 and 69, but a prediction that this feature be responsible for the apparent complete suppression of photoisomerization would have been difficult. Stereoelectronic factors (in conjunction with the substituent at C-2 in both ketones) and the cross-conjugation (in 84) may possibly play an important role in these systems⁴³. Lack of material and time did not allow further experimentation. In particular, a check for predominance of back reaction, 117 $\rightarrow$ 75 and 118 $\rightarrow$ 84, could not be carried out.

Triplet sensitization under similar conditions as used for 68, were carried out with 69, 75, 83 and 84 using benzophenone ($E_T=68$ kcal/mol), and with 83 and 84 also using acetone ($E_T=80$ kcal/mol). Only 69 and 75 underwent the ODPM rearrangement to products 119 and 120, respectively. 83 and 84 remained unchanged with only little degradation of starting material after ca. 100 hours of irradiation.

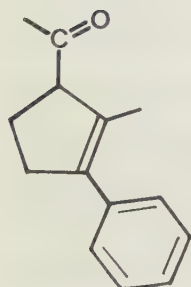
In the NMR spectrum of the crude reaction mixture of 69 only one isomer was observed (a singlet each at δ 2.17 for COCH_3 and at δ 1.30 for the $\beta\text{-CH}_3$; no olefinic proton) which, when compared with the NMR data of the acetylbicyclopentanes 98a and 98b, appears to correspond to the endo-configuration. The structure assignment to the triplet product of 75 is also based solely on the NMR data of the crude reaction mixture showing two singlets at δ 1.47 and 1.53 for the $\alpha\text{-CH}_3$ in a ca. 1:1 ratio (suggesting an endo/exo mixture) and one singlet at δ 2.02 for COCH_3 , and lacking any signal for olefinic protons.



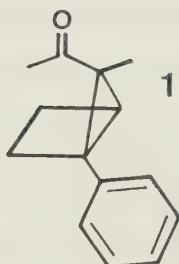
69



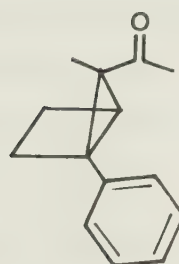
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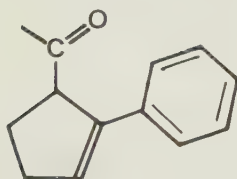
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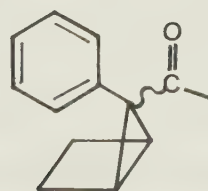
120a



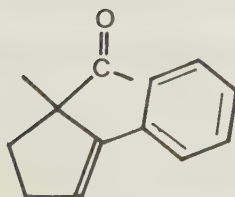
120b



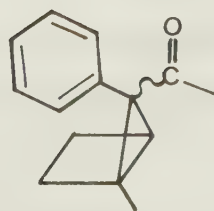
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121

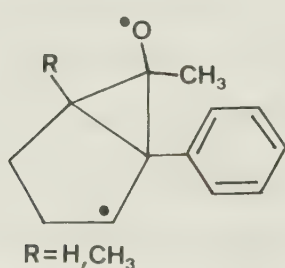


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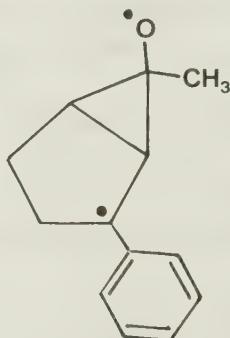


122

The failure of ODPM rearrangement in 83 and 84 might be due to steric hindrance in the diradical intermediate⁴², caused by the interaction of the β -phenyl substituent and the methyl or the oxyradical (see 123; only one diastereoisomer shown). Another factor could be that in the bonding step to 123 the styrene π -system is separated into phenyl and an isolated secondary radical site, whereas in the analogous process affording 124 the two groups remain resonance-stabilized. (Note that in the similar reaction step 4 $\rightarrow$ 51 the isolated radical is formed with much less sacrifice of π -conjugation than in 83, 84 $\rightarrow$ 123).

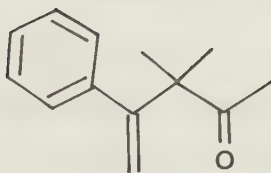


123



124

The non-reactivity of 83 and 84 may be related to Dauben's⁶⁰ case of compound 125, which upon sensitized irradiation does not undergo any structural transformation either. This result has been ascribed to the position of the substituent as well as little or no $n \rightarrow \pi^*$ enhancement ($\epsilon \frac{42}{293} = 376 / \epsilon \frac{125}{291} = 11$; cf. $\epsilon \frac{68}{300} = 1500 / \epsilon \frac{83}{300} = 650$; $\epsilon \frac{69}{300} = 1200 / \epsilon \frac{84}{300} = 183$).



125

Since the ODPM rearrangement products of the acetylcyclopentenes are known to be thermally unstable, the lack of triplet-product formation from 83 and 84 might also be due to instantaneous thermal isomerization of 121 and 122 back to the starting materials. However, 1-phenylcyclopropyl methyl ketone (13) is thermally stable. Sensitized photolyses at low temperature have not been carried out.

2. The Thermal Isomerization of 1-Phenyl-5-acetylbicyclo[2,1,0]pentane

From earlier work by Baggiolini⁶, Gonzenbach⁵, Jorgenson⁶¹ and Grosclaude⁴⁸ it is well known that the triplet photoproducts of the acetylcyclopentenes are thermally reversible to starting material and the 1,3-acyl shifted product. Kinetic studies⁴⁸ of endo- and exo-5-acetyl-5-methylbicyclo[2,1,0]pentanes have provided a clear mechanistic differentiation between the endo-exo inter-

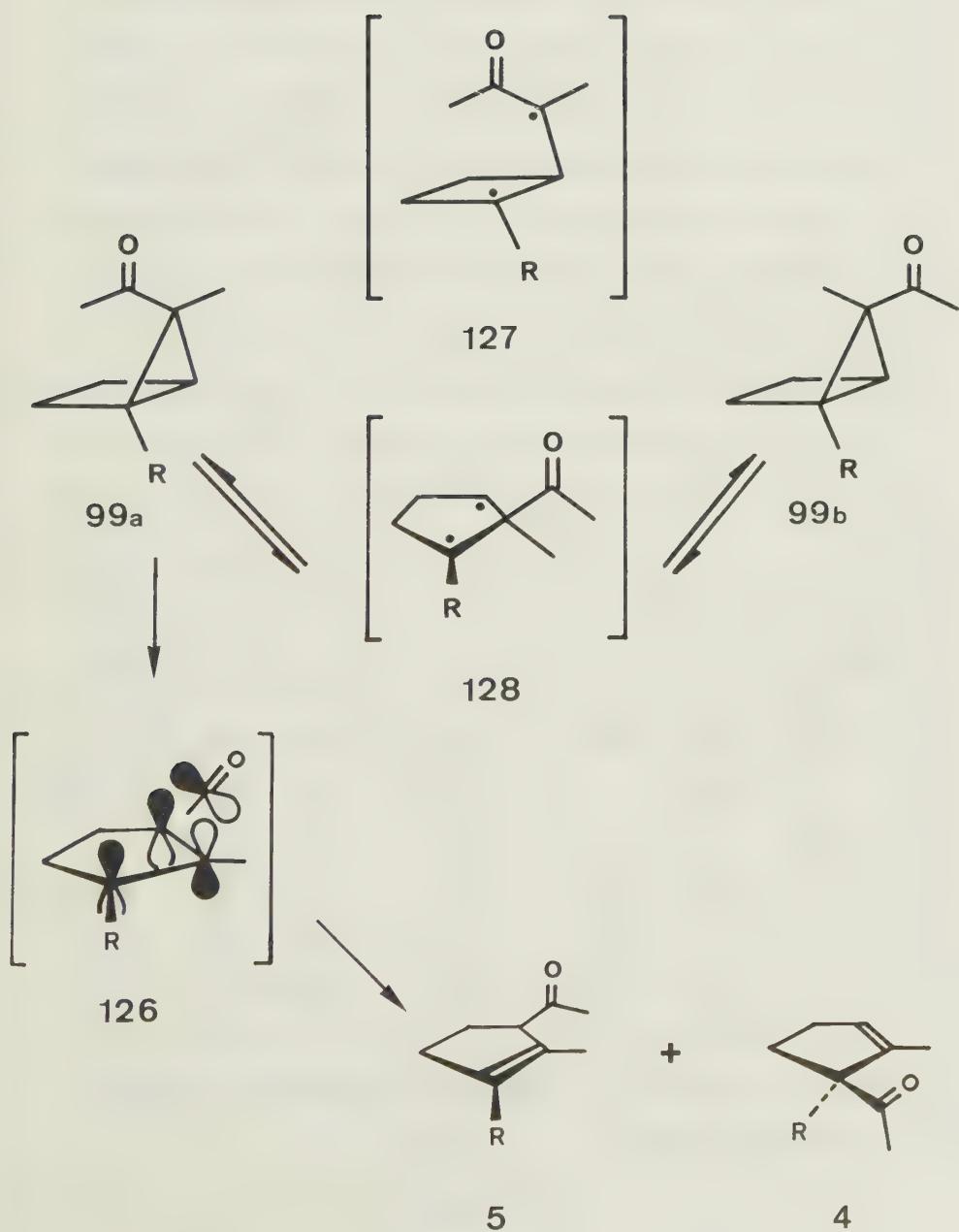
conversion and the cyclopropyl-allylic rearrangement. Rate constants in the order $k_{\text{endo-exo}} > k_{\text{exo-endo}} > k_{\text{endo rearrangement}} \gg k_{\text{exo rearrangement}}$ and significantly different activation parameters preclude a common intermediate for the two reactions and also show that the rearrangement occurs exclusively from the endo-isomer. A large negative entropy of activation is suggestive of an electrocyclic process of the latter reaction via a thermally allowed four-electron Möbius-type transition state (126). This reaction path could thus involve an anti-disrotatory opening of the internal cyclopropane bond and a 1,2-acetyl shift in a concerted manner.

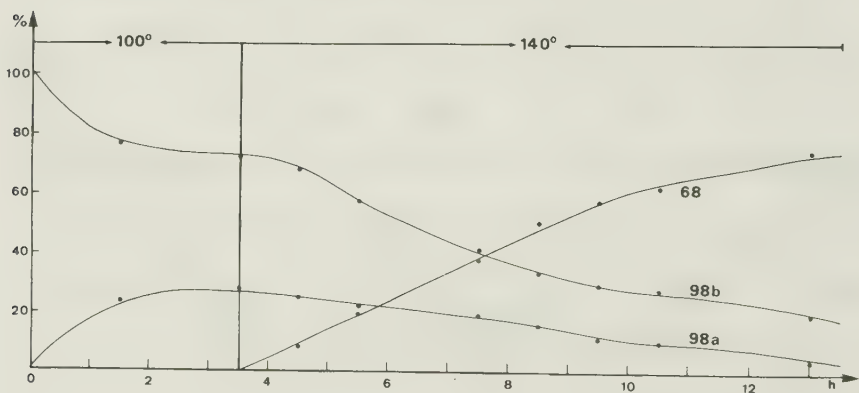
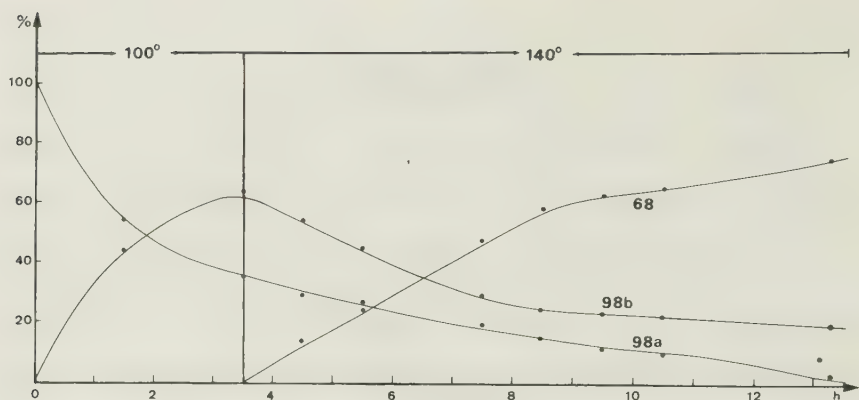
From a chiroptical analysis⁴⁸ it was shown, furthermore, that the stereomutation involves exclusively the diradical intermediate 128. These results are summarized in Chart 6.

Separate thermolyses of the endo- and exo-bicyclopentanes 98a and 98b were carried out in sealed tubes at 100° and 140°. The following data were obtained by NMR analysis in deuterated benzene solutions only, and include relatively large errors owing to the method used. VPC-analytical conditions could not be found to separate the endo- and exo-isomers. The product compositions of the pyrolyzed mixtures are represented as a function of reaction time in Figures 4 and 5 and Table IV.

In view of the analytical difficulties mentioned, the curves in Figures 4 and 5 should only be assessed by visual inspection rather than by a more elaborate analysis. Even so, the trends of the curves are sufficiently differentiated to demonstrate beyond doubt that only reactivity relationships as shown in Chart 6 with an order of rate constants $k_{12} > k_{21}$ and $k_{13} > k_{23}$ can satisfactorily

Chart 6

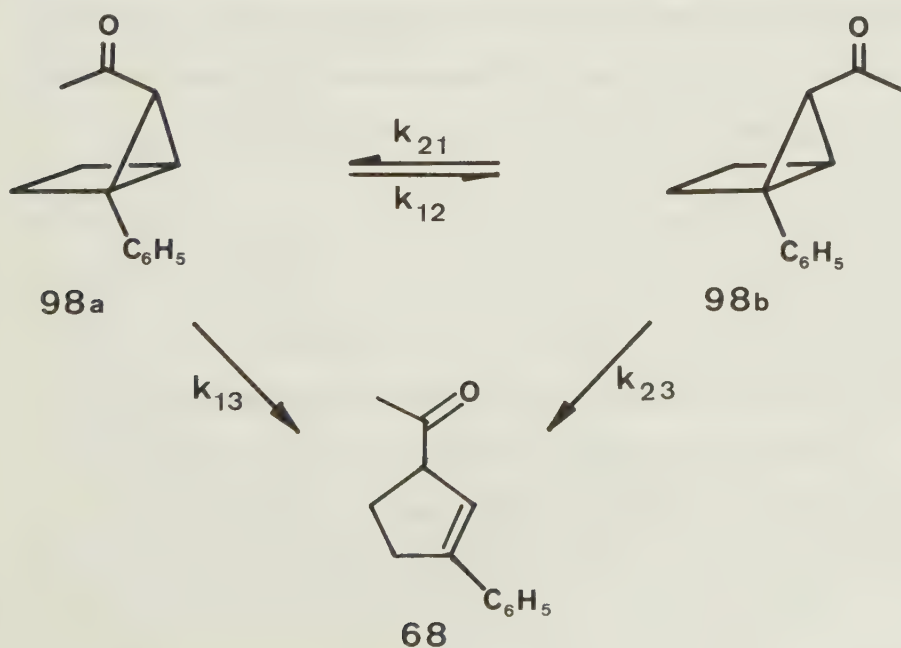




Thermolysis of endo-98a			Thermolysis of exo-98b			
%98a	%98b	%68	hours	%98a	%98b	%68
45	55		1.5	24	76	
36	64		3.5	28	72	
30	55	15	4.5	25	68	7
28	46	26	5.5	22	58	20
20	30	50	7.5	20	42	38
15	25	60	8.5	16	34	50
12	24	64	9.5	12	30	58
10	23	67	10.5	10	28	62
5	20	75	13.0	5	20	75

Figure 4 and 5 and Table IV: Concentration/time dependence for thermolysis of endo-98a and exo-98b.

account for these results. In other words, the pattern of reaction paths and preferences is quite analogous to that established rigorously by Grosclaude et al.⁶² for the nonphenylated acetylbicyclopentanes. Again the *exo* configuration prevails in the equilibrium of the stereomutation, and the allyl-cyclopropyl rearrangement occurs at least selectively from the *endo* isomer. A common intermediate in the formation of all three compounds is thus very unlikely and possibly again inexistent. The latter point is in fact particularly well documented by the fact that at 100° no rearrangement to 68 could be detected in the *endo-exo* equilibration. The appearance of 68 became only detectable when the temperature was raised to 140°. This is explicable when the two processes, stereomutation and allyl-cyclopropyl rearrangement, occur on different potential energy surfaces and if the rearrangement requires an activation energy higher than that provided for at 100°.



From a mechanistic point of view the stereomutation may involve either or both of the two diradicals 129 and 130 (Chart 7). Breaking of the C_1-C_5 bond would give the diradical 129 which is free to rotate (given the necessary activation to overcome the steric inhibition; cf. the discussion on page 59) and reclose. The "ring flip" via the cyclic diradical 130 is the alternative for steric equilibration. Attempts have been made to scavenge the diradical(s) with dimethyl acetylene dicarboxylate, but no intermediate could be trapped this way. A direct analysis of the reaction path(s) followed would be possible by a study of optically active 98a and 98b, but has not yet been undertaken. We should recall that this approach proved successful in the study by Grosclaude (cf. Chart 8). As can be seen from the representation in Chart 7 the allyl-cyclopropyl rearrangement from the endo isomer 98a requires a significantly smaller geometrical change on the concerted pathway than the exo compound, which accounts for the stereoselective reactivities of the two acetylbicyclopentanes. The reaction coordinates in Figure 6 summarize the thermochemical relationships, as defined by the experimental results, between the three isomers 68, 98a and 98b.

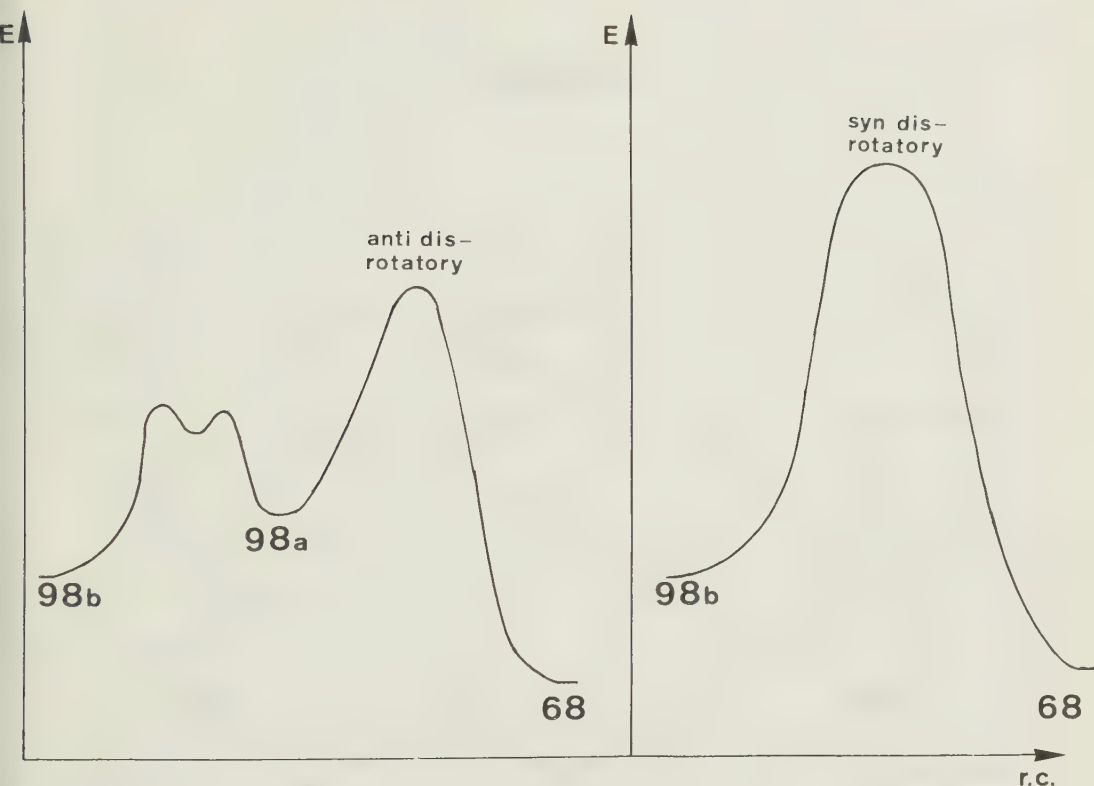


Figure 6: Reaction Coordinates of the Thermal endo/exo Stereomutation (98a → 98b) and the cyclopropyl-allylic rearrangement(98a → 68)

The result of the thermal rearrangement of 98a differs qualitatively in one aspect from the Grosclaude series: In the latter the products of both possible directions of acetyl migration are observed, with the rearrangement towards the more highly substituted allylic carbon predominating. In contrast, 98 yields only 68 and no trace of 92 could be detected, which would correspond to the major product in the non-phenylated series. A possible rationalization, although perhaps hazardous, may be attempted here. Without prejudicing an eventual differentiation between

Chart 7

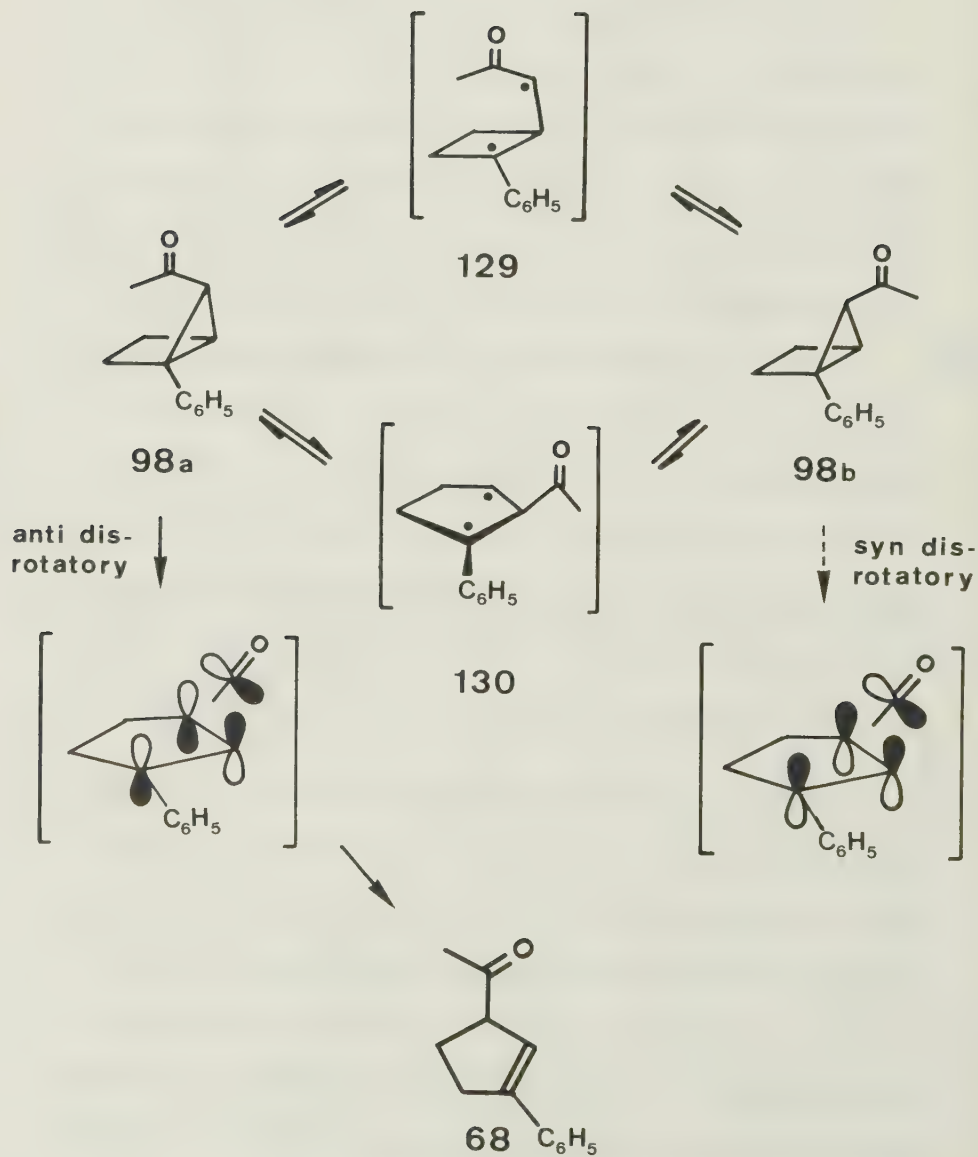
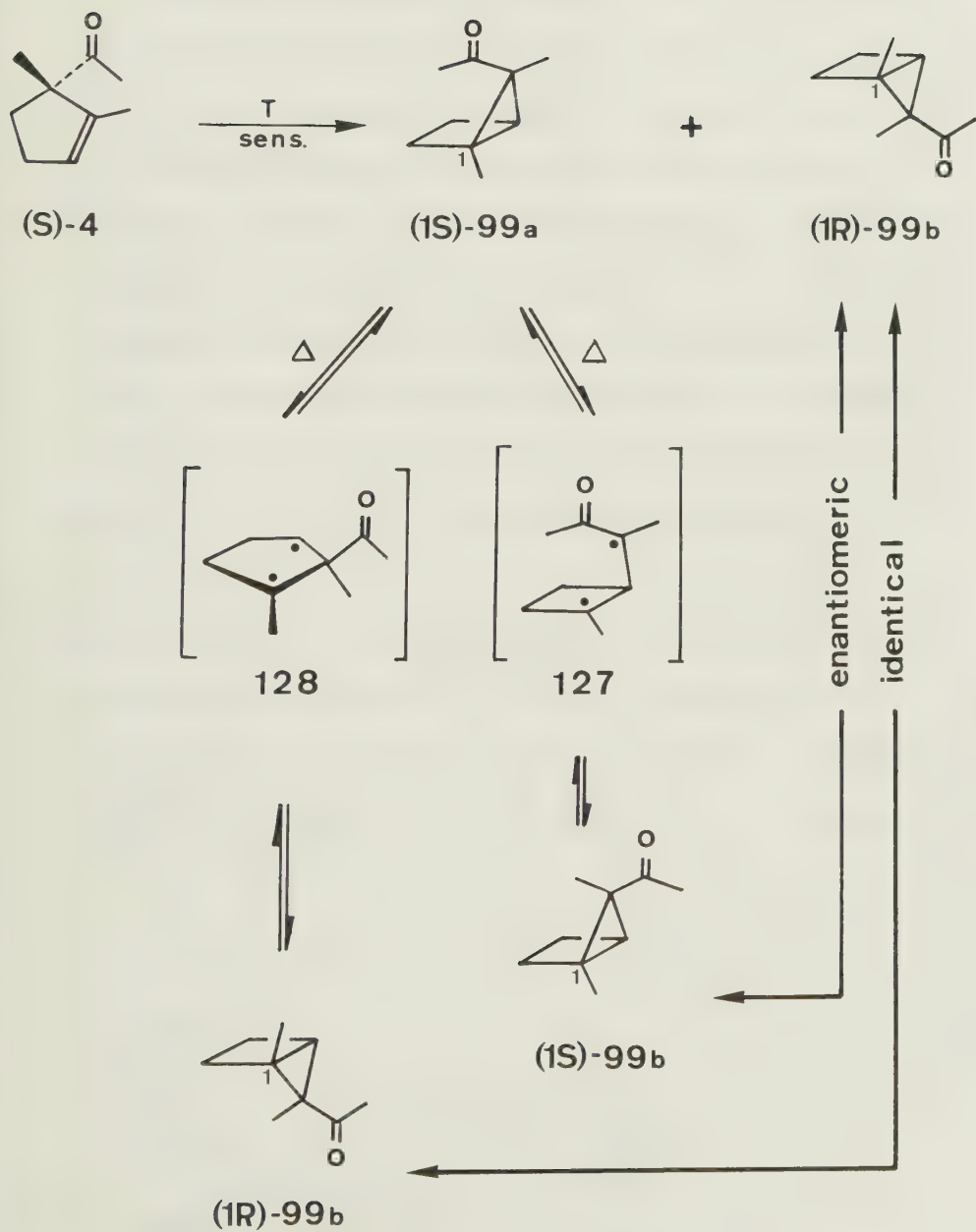


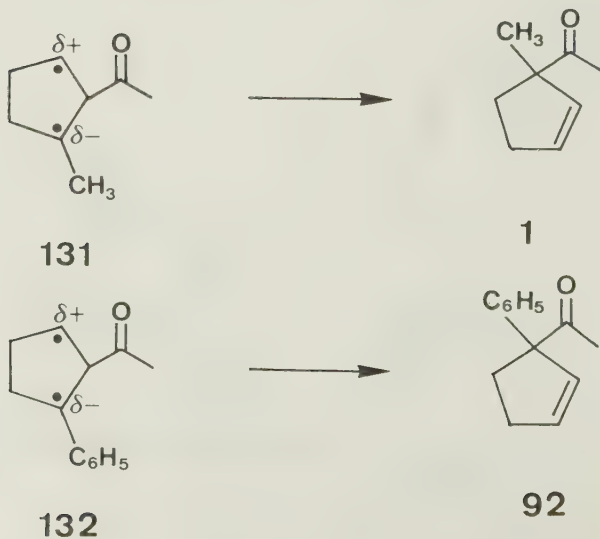
Chart 8



stepwise and concerted mechanism in the present study, let us consider the two formally possible (in the case of $\underline{99} \rightarrow \underline{4}$ experimentally rejected) intermediates $\underline{131}$ and $\underline{132}$. In $\underline{131}$ both the inductive and the resonance stabilization (hyperconjugation) effects render the tertiary radical more electronegative than the secondary site, which would readily explain the observed preference for formation of $\underline{1}$. In the phenyl series the resonance stabilization is definitely much more important than any induction which may be exerted by the phenyl on the radical site, and the resonance stabilization would favor a polarization as indicated in $\underline{132}$ corresponding to the situation required for the formation of the sole product ($\underline{68}$) in this case. These arguments are, of course, not only valid for the representation chosen in Chart 9, but they can also be applied to the corresponding transition states in concerted mechanisms.

Chart 9

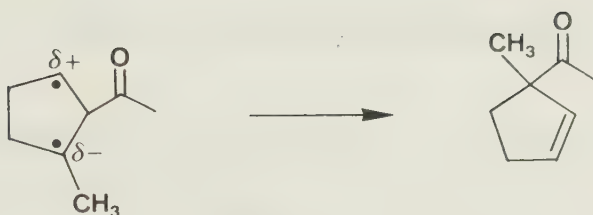
inductive
stabilization
effect:



resonance

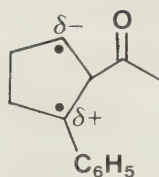
stabilization

effect:



131

1



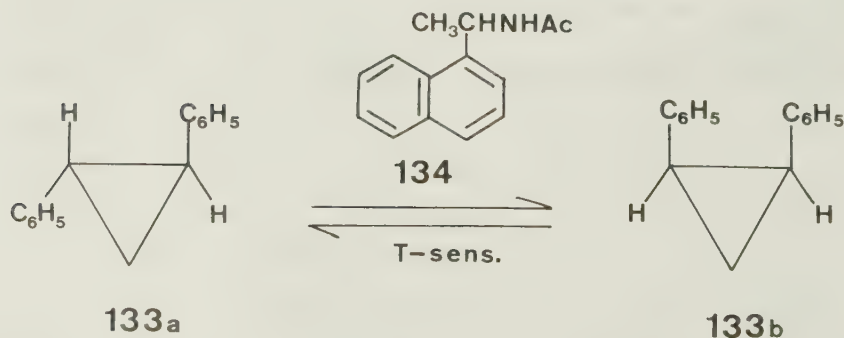
132

68

Differences due to the resonance stabilization effect, if present, should be more pronounced with electron-donating and electron-withdrawing p-substituents on the phenyl group. E.g., cyano and nitro groups would favor the formation of the corresponding 1-aryl-3-acetyl-1-cyclopentenenes, and a methoxyl should reverse the situation and favor 1-p-anisyl-1-acetyl-2-cyclopentene. The synthesis and study of these compounds is presently in progress.

3. Asymmetric Induction in Triplet Sensitization

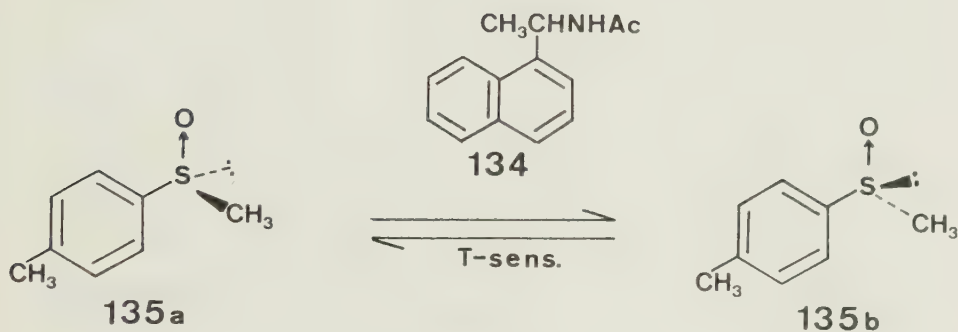
If transfer of triplet excitation follows the exchange mechanism, i.e. if molecular contact between donor and acceptor is required, stereochemical factors should be of importance in determining the efficiency of transfer. This expectation has in fact been met in several systems where steric crowding of the acceptor and donor chromophores proved to lower the transfer efficiency⁶³. One might anticipate that an optically active sensitizer (donor) would be able to show selection between the enantiomers of a chiral acceptor. This field has been studied very little. The first example was provided by Hammond and Cole⁶⁴ with an asymmetric induction during the isomerization of *trans*-1,2-diphenylcyclopropane 133a using the optically active naphthalenic sensitizer 134. The optical yield is not known and the mechanism in this case rather indicates singlet energy transfer via exciplex formation⁶⁵.



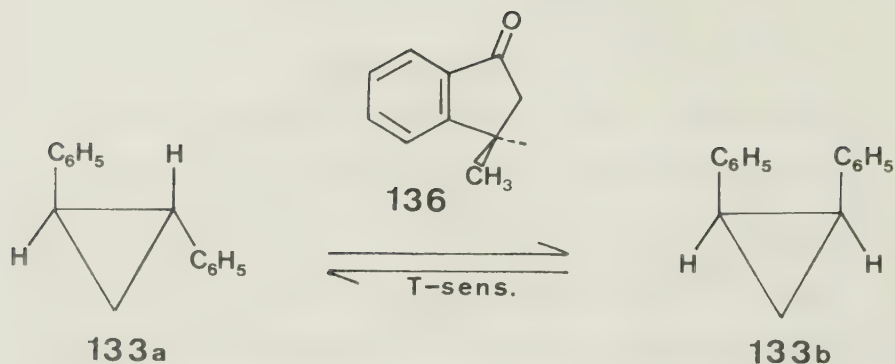
A similar asymmetric induction via exciplex has been studied by Kagan^{66, 67}.

Racemic methyl-*p*-tolyl sulfoxide 135a was irradiated in the presence of the

sensitizer 134 resulting in a sulfoxide with an optical purity of $2.20\% \pm 0.25\%$.



Ouannes⁶⁸ reported a case of exothermic energy transfer to trans-1,2-diphenylcyclopropane 133a from the optically active 3-methyl-1-indanone (136). The optical rotation of trans-1,2-diphenylcyclopropane (133) after irradiation was found to be $+12.4^\circ$, which corresponds to an asymmetric synthesis of 3%. In the transfer step the preferential orientation of the sensitizer with one enantiomer of the substrate to allow for maximum π overlap was suggested. This implies that the two diastereoisomeric encounter complexes differ with respect to transfer efficiency.

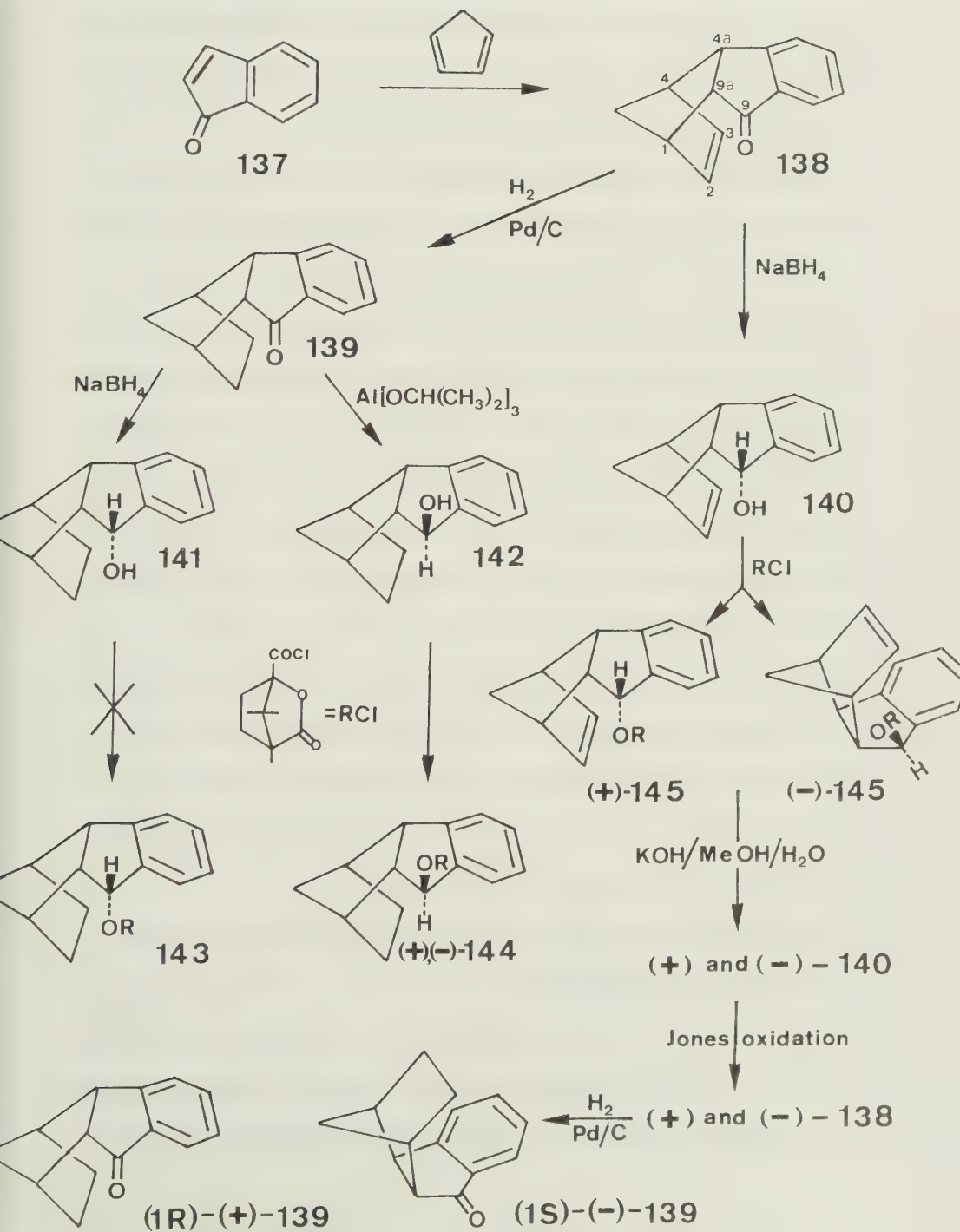


3.1. Synthesis of an Optically Active Indanone Sensitizer

(Chart 10) The racemic crystalline indanone 138 was prepared by the addition of indenone⁶⁹ to cyclopentadiene in 93% yield after column chromatography on silicagel. Only one isomer, derived from Diels-Alder-type endo-addition was obtained. It was catalytically hydrogenated to give a 90% yield of 139 after recrystallization.

The optical resolution was achieved by column-chromatographic separation of the diastereomeric esters 145 (IR: 1728 and 1745 cm^{-1}) obtained from (-)-camphanic acid chloride⁷⁰ with the racemic endo-alcohol 140. The diastereoisomers 145

Chart 10



showed optical rotations of $[\alpha]_D = +87.0^\circ$ and -88.8° and a diastereoisomeric purity of ca. 92% from NMR analysis. Crystalline 140 had been obtained from stereoselective reduction of 138 with sodium borohydride in 95% yield after crystallization. Stereoselection was also observed in the NaBH_4 reduction of the dihydro adduct 139 giving the endo-alcohol 141 in 50% yield, whereas the exo-isomer 142 was obtained in 80% yield by aluminumisopropoxide reduction of 139 in toluene⁷¹. However, 141 could not be esterified to 143, most probably due to steric hindrance by the endo- C_2 and -C_3 protons. The exo-alcohol 142 gave the diastereoisomeric esters 144, but this path was abandoned since the ketone reduction was less efficient here than in the unsaturated series 138 $\rightarrow$ 140. Basic hydrolysis of the separated esters (+)-145 and (-)-145 gave in quantitative yield the enantiomeric alcohols (+)-140 (m.p. 136° , $[\alpha]_D = +230^\circ$) and (-)-140 (m.p. 137° , $[\alpha]_D = -231^\circ$), respectively. Oxidation of (+)-140 and (-)-140 with Jones reagent afforded after column chromatography and recrystallization the ketones (+)-138 and (-)-138 in 90% yield each (m.p. $75\text{--}76^\circ$ for both, $[\alpha]_D = +56.5^\circ$ and -56.4° , respectively). Catalytic hydrogenation finally resulted in a quantitative yield of the desired optical active ketones (+)-139 (from (-)-138; m.p. $58\text{--}60^\circ$, $[\alpha]_D = +67.7^\circ$) and (-)-139 (from (+)-138; m.p. $61\text{--}62^\circ$, $[\alpha]_D = -68.4^\circ$).

Adduct 138 shows a carbonyl band at 1720 cm^{-1} in the IR spectrum. The NMR exhibits an AB quadruplet for the two bridge protons at δ 1.29 and 1.41. The coupling constant of 12 Hz is in accordance with the value for the corresponding protons in norbornane. Furthermore, the NMR of 138 exhibits a complex system of three protons at δ 3.06–3.82, a doublet-of-a-doublet of one proton at about

δ 3.85, the A parts of two AA'M systems at δ 5.44 and 5.86 of the olefinic protons at C-2 and C-3, and a complex multiplex of the aromatic protons at δ 7.30-7.60. Identification of the six protons at C-1, -2, -3, -4, -4a and 9a was carried out by chemical shift analysis followed by decoupling experiments. With $\text{Eu}(\text{FOD})_3$ as a shift reagent the deshielding properties in relation to increasing concentration of shift reagent are represented in Fig. 7 for each of the six protons. From the slopes $\frac{\Delta \delta}{\Delta [\text{Eu}]}$ one can deduce their distance in space to the carbonyl oxygen in the order $9a\text{-H} < 1\text{-H} = 2\text{-H} < 4a\text{-H} < 3\text{-H} = 4\text{-H}$. The similarity of the slopes of 1- and 2-H in 138 provides evidence for the endo-configuration of the compound. If the exo-isomer was present instead, the deshielding of 2-H and 3-H should be very similar due to their similar environment. Additional information in favor of the geometry derives from the bridge protons. They show both the same shift with increasing amount of $\text{Eu}(\text{FOD})_3$ which indicates that they are both far from the carbonyl group. The three-proton system at δ 3.06-3.82 was resolved by shift reagent analysis into one doublet-of-a-doublet for 9a-H and two almost identical multiplets for 1-H and 4-H. Irradiation at one or the other of the bridgehead protons reduced the multiplet of one of the olefinic protons at a time into a doublet; $J_{2,3}=5.5$, $J_{3,4}=2.3$ and $J_{1,2}=2.7$ Hz. Furthermore, the same irradiation resolved also 4a-H and 9a-H into doublets; $J_{4a,9a}=6$ Hz proves the cis-geometry of these protons, and $J_{1,9a}=J_{4,4a}=4.6$ Hz is in agreement with the similar constant in norbornene, with "9a-H" corresponding to an exo-methylene proton.

The endo- and exo-assignment to the hydroxyls of the alcohols 140, 141 and 142 are based on the coupling constant $J_{9,9a}$ which is 9 Hz for the endo-alcohols

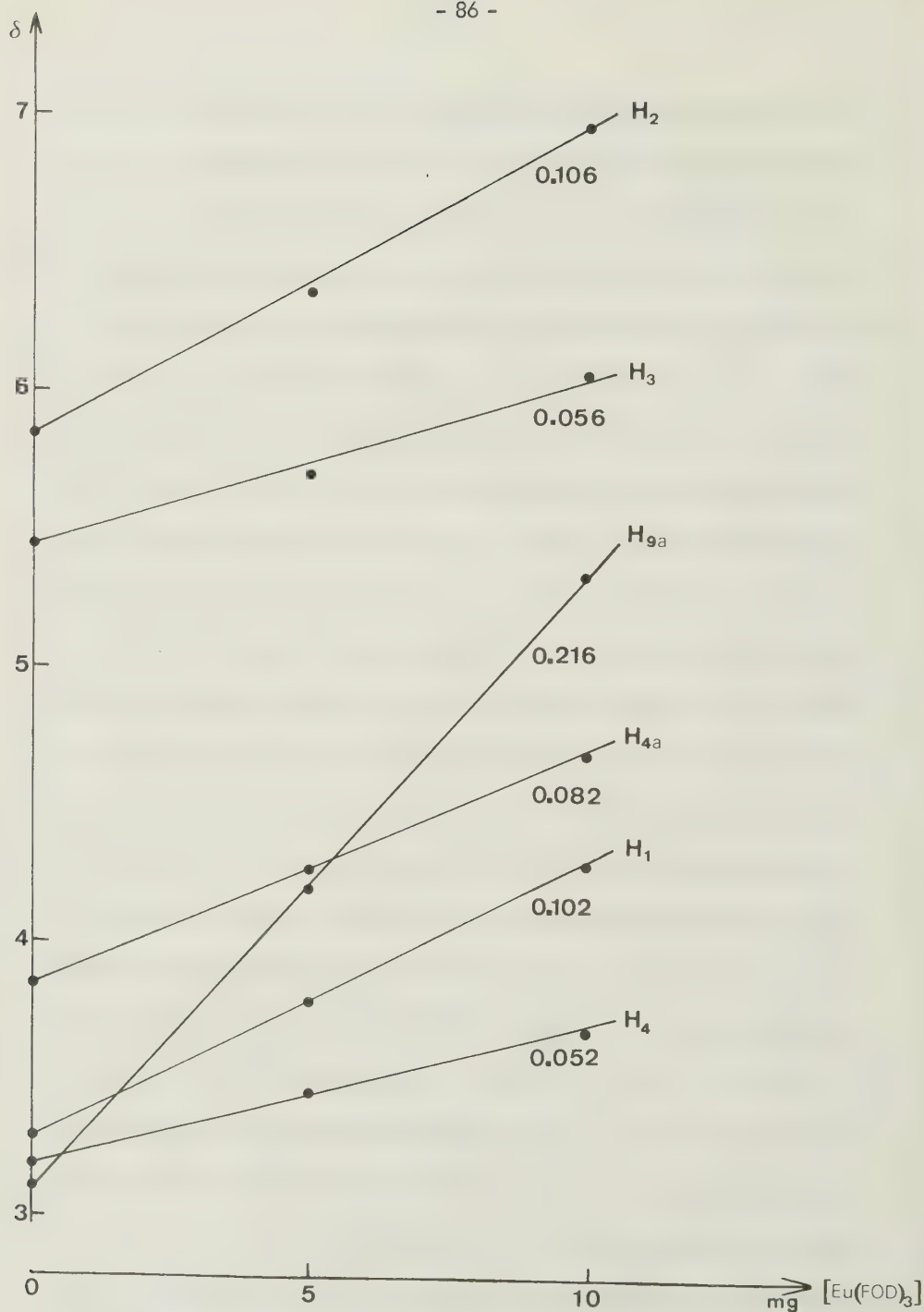
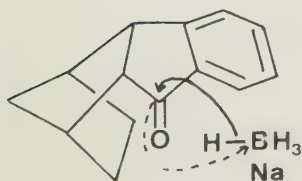


Figure 7: Proton Deshielding versus $[\text{Eu}(\text{FOD})_3]$ for 138

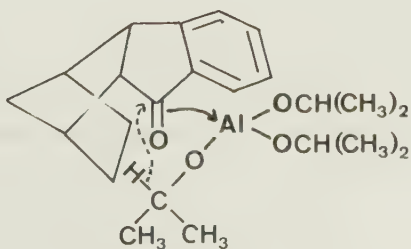
$$\text{indicated numbers} = \frac{\Delta \delta}{\Delta [\text{Eu}]}$$

140 and 141 and 0 Hz for the exo-epimer 142. These values are in good agreement with a cis-9-H/9a-H geometry possessing dihedral angles of close to 0° in the endo-alcohols and ca. 110° in the exo-alcohol. Irradiation at 9a-H in 140 and 141 reduces the 9-H doublet to a singlet broadened by small coupling with the hydroxylic proton. These secondary alcohols show a sharp non-associated band at ca. 3600 cm^{-1} in the IR spectrum.

The result of the reduction step from ketones 138 and 139 to the endo- and exo-alcohols need to be commented. The opposite stereoselectivity of the hydride and the Merwein-Ponndorf-Verley reductions conforms to the combined effects of the reaction mechanisms and the differences exhibited by the steric crowding of the ketone groups in 138 and 139. The dihydro compound 139 is more strongly shielded against endo-attack on the carbonyl by the endo-methylene protons and therefore forces the kinetically controlled hydride addition to occur from the exo-side affording the more hindered endo-alcohol 141 (cf. 146). The same epimer is obtained from hydride reduction of the unsaturated compound 138, since the exo side is here still the most accessible. In contrast, thermodynamic equilibration, characteristic for the reduction with alkoxides, leads from 139 to the less hindered exo-alcohol 142 (cf. 147).



146



147

(-)-Ketone 139 exhibits in the circular dichroism two negative Cotton effects in the aromatic region and a progression of positive Cotton effects in the region of the $n \rightarrow \pi^*$ transition (see Table V). This circular dichroism is quite similar to that described, e.g., for the 1-indanone (+)-148, by Marquet et al.⁷², and the (1*S*,4*R*,4*aS*,9*aS*)-configuration as shown in the formulas can therefore be assigned to (-)-139 on this basis.

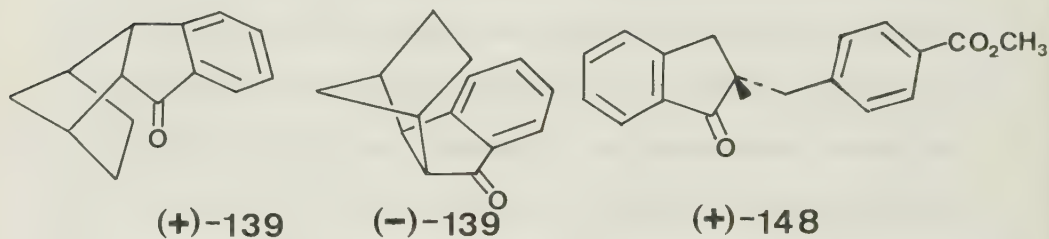


Table V: Circular Dichroism of Ketone (-)-139:^{a)} Maxima and intersection (i) with λ Axis

λ , nm	$\Delta\epsilon$
284.5	- 5.11
294.0	- 5.75
311.0	+ 0.46
323.5	+ 0.78
337.5	+ 1.01
353.5	+ 0.82
370.0	+ 0.32
301.0 (i)	0

a) solvent: cyclohexane; concentration: 0.113 mg/ml; temperature: 24°

Compound 139 belongs to a series of indanone species which exhibit anomalous luminescence properties in EPA at 77K^{13, 73}, i.e. a dual phosphorescence with nonexponential lifetime decay. This feature has been observed earlier for 1-indanone⁷⁴, but the origin of the anomaly has remained a matter of discussion⁷⁵. The indanone dual phosphorescence was assigned to n, π^* and π, π^* short- and long-lived emission, respectively, and was attributed to a failure of the two essentially isoenergetic triplet states to rapidly equilibrate at 77K ($E_T = 74$ kcal/mol)⁷⁶. A lack of sufficiently close-lying vibrational levels in the two energetically almost degenerate triplet configurations has been postulated to account for the lack of such equilibrium. Our findings, which include different excitation spectra for the short- and long-lived phosphorescence, are interpreted in terms of selective population of the two emitting triplet states^{13, 73}. Figure 8.

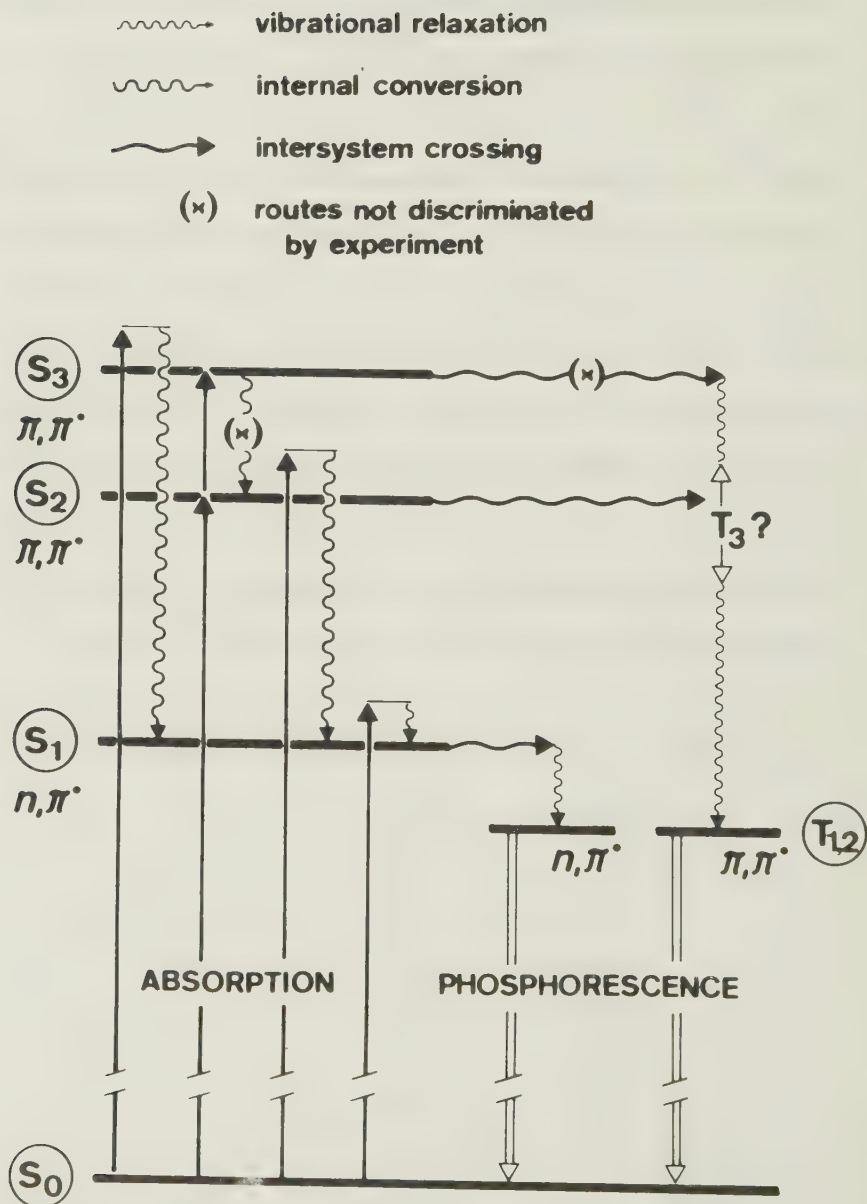
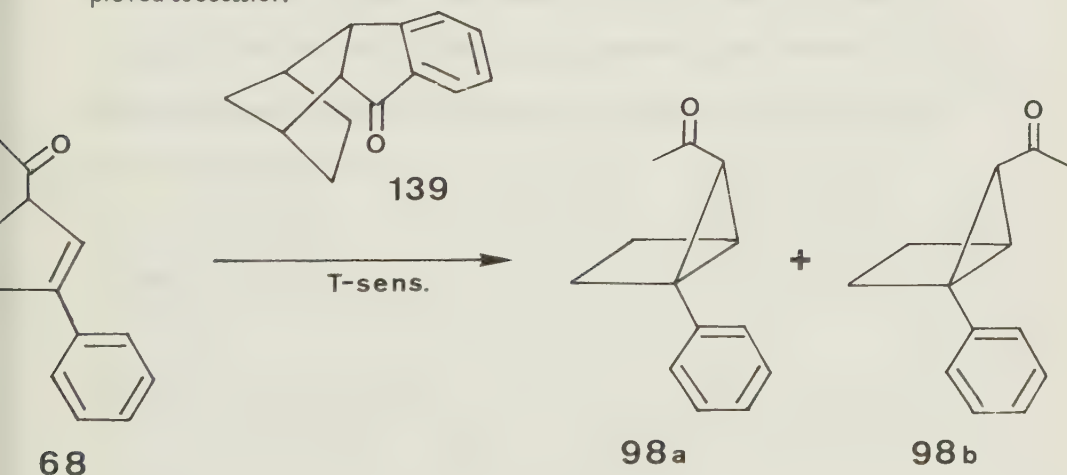


Figure 8: State diagram of indanone with preferred internal conversions and intersystem crossing processes (in EPA at 77K).

3.2. Preliminary Sensitization Experiments

With (1S)-(-)-139 at hand, a preliminary search was undertaken for a donor-acceptor system which would fulfill simultaneously the energetic requirements of exothermic triplet-triplet transfer and a topological matching of the chromophoric moieties of the collision partners in such a way as to favor specifically one diastereoisomeric arrangement in the encounter complex.

Sensitization of the ODPM rearrangement of 1-phenyl-3-acetyl-1-cyclopentene (68) with ($\pm$)-139 to the endo- and exo-acetylbicyclopentanes 98a and 98b proved successful.



We expected now that the most efficient interaction between donor and acceptor should occur by sandwich-like π -overlap of the phenyl ketone and the styrene chromophores and that the asymmetrically attached acetyl sidechain of 68 might exert sufficient steric discrimination to induce asymmetrical sensitization.

Irradiation at > 340 nm of a benzene solution of 68 at room temperature in the presence of (-)-139 resulted, however, in a mere optical rotation of about -3°

of the bicyclic ketones 98a and 98b after 40% conversion of starting material. Even more significant, the recovered starting material exhibited no worthwhile optical activity ($[\alpha]_D = -1.5^\circ$). A similar experiment in toluene solution was carried out also at -100° , since one would expect more efficient orientation at reduced diffusion rates, but no increase in optical rotation of the products was noticed. Although the enantiomeric purity of the product components has not been determined, the overall result does not seem encouraging.

One possibility for a greater optical induction in this system might be to increase either the electron-donor ability of the sensitizer by p-nitro or p-cyano substitution or the electron acceptor ability of the substrate by p-methoxy substitution. In this way perhaps a charge-transfer ground state and creation of an excited complex concomitant with a greater orientational effect could eventually be enforced.

4.

Experimental Part

4.1. General Remarks

UV absorption spectra (Beckman-Acta-III) are given in nm, with the respective molar extinction coefficient ϵ in brackets. Solvent: isooctane.

IR spectra (Perkin-Elmer 257-IR) are given in wavenumbers (cm^{-1}). Intensities: s = strong, m = medium and w = weak. Solvent: CCl_4 unless specified.

^1H -NMR spectra (Varian -XL, 100MHz, Perkin-Elmer R-12, 60MHz and T-60) were measured with TMS as internal standard and CDCl_3 as solvent unless specified. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz. Signal characteristics: s = singlet, d = doublet, t = triplet and m = multiplet of higher than first order.

Mass spectra (Varian SM-113) in m/e units. The molecular ion is followed by the elemental composition. The base peak is underlined.

Optical rotations (Perkin-Elmer-141 polarimeter) were measured in a 10 cm cell in CHCl_3 ; concentration c added in parentheses.

For thin layer chromatography Merck prepared plates with fluorescence indicator were used. The spots were traced by UV light, sprayed with concentrated sulfuric acid and heated.

Column chromatography: Merck silica gel, size 0.05-0.2 mm.

Vapor phase chromatography: Perkin-Elmer 990. Packed steel columns 2,5 m x 4 mm with 5% and 15% SE 30 on Chromosorb W-HP. Carrier gas: Helium 80-150 ml/min.

Detector system FID. Integration: Electronic integrator Infotronics CRS-208F.

Phosphorescence emission spectra were run on a modified Fica-55 spectro-photometer at 77 K in EPA (ether-isopentane-ethanol 5:5:2).

Usual work-up means: The reaction mixture was extracted with ether, washed neutral with water and saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and the solvent was evaporated under vacuum in a rotary evaporator.

The following abbreviations are used for solvents: EA = ethyl acetate, Tol = toluene

I should like to thank Miss Veronique Martinez and Mr. Felici Andreoli for their technical help in the laboratory work.

4.2. Synthesis of the Acetyl-phenylcyclopentenones 68, 69, 75, 83 and 84 (Charts 2 and 3)

Acrylic esters by the modified Wittig reaction

1.6 eq. of NaH 50% were suspended in diglyme or glyme. To this slurry were added dropwise 1.6 eq. of diethylphosphonoacetate or propionate at 25°. When the hydrogen evolution had stopped, 1.0 eq. of aldehyde 61 or ketones 71 or 76 was added dropwise at room temperature. The reaction mixtures with glyme were refluxed for 2 days and those with diglyme were stirred at 80° overnight before the temperature was raised 20° per day until reflux set in (160-165°) which was maintained for at least another 2 days. The reactions were followed by TLC with Tol-EA 4:1. The reaction mixtures were then poured onto water, followed by the usual work-up and distillation.

Ethyl (E)-3-(1-phenylcyclopropyl)-acrylate (62)

25.0 g (0.12mol) of 61²⁸ and 61.0 g (0.23mol) of phosphonoacetate afforded 18.1 g (50%) of pure (E)-ester after two days of reflux in glyme; b.p. 85°/0.08 Torr.

UV: 225 (6500). IR: 1720 s. MS: 216 ($C_{14}H_{16}O_2^+$), 188, 143. NMR; CCl_4 : 1.05/m $-CH_2CH_2-(cyclopropyl)$; 1.23/t J=7, $CH_3(ester)$; 4.35/q J=7, $CH_2(ester)$; 5.18/d J=15, 2-H; 6.60/d J=15, 3-H; 7.18/s ArH.

Ethyl (E+Z)-2-methyl-3-(1-phenylcyclopropyl)-acrylates (63)

3.65 g (0.025mol) of 61²⁸ and 10.0 g (0.04mol) of diethylphosphonopropionate in glyme gave after 2 days of reflux a mixture of the (E+Z)-esters in 50% yield (2.6 g), E:Z=6:1; b.p. 99°/0.17 Torr.

UV: 212 (5800) for (Z), 226 (7500) for (E). IR: 1728 s for (Z), 1710 s for (E), 1608 m. MS: 230 ($C_{15}H_{18}O_2^+$), 202, 173, 157. NMR; CCl_4 ; for (E): 1.16/m $-CH_2CH_2-(cyclopropyl)$; 1.15/d J=1.5, 2- CH_3 ; 1.25/t J=7, $CH_3(ester)$; 4.17/q J=7, $CH_2(ester)$; 6.85/q J=1.5, 3-H; 7.20/s ArH. For (Z): 1.00/m $-CH_2CH_2-(cyclopropyl)$; 1.10/t J=7, $CH_3(ester)$; 1.88/d J=1.5, 2- CH_3 ; 3.95/q J=7, $CH_2(ester)$; 5.93/q J=1.5, 3-H; 7.10/s ArH.

Ethyl (E)-3-(1-phenylcyclopropyl)-2-butenolate (72)

5.1 g (0.03mol) of 71 and 11.2 g (0.05mol) of phosphonoacetate gave after 4 days reflux in diglyme 3.5 g (48%) of (E)-ester; b.p. $125^{\circ}/1$ Torr.

UV: 235 (9100). IR: 1722 s, 1650 m. MS: 230 ($C_{15}H_{18}O_2^{+}$), 202, 173, 157.

NMR; CCl_4 : 1.07/m $-CH_2CH_2-(cyclopropyl)$; 1,21/t J=7, $CH_3(ester)$; 2.02/d J=2, CH_3-4 ; 4,05/q J=7, $CH_2(ester)$; 5,60/q J=2, 2-H; 7,09/s ArH.

Ethyl (E+Z)-3-phenyl-3-cyclopropyl acrylates (77)

8.9 g (60%) of a 1:1 mixture of esters 77, b.p. $90^{\circ}/0.1$ Torr, were obtained from 10.0 g (0.07mol) of 76 and 27.7 g (0.12mol) of phosphonoacetate.

UV: 209 (5800) for (Z), 241 (4700) for (E). IR: 1735 s for (Z), 1720 s for (E), 1635 m. MS: 216 ($C_{14}H_{16}O_2^{+}$), 188, 143. NMR; CCl_4 ; for (E): 0,69/m $-CH_2$

$CH_2(cyclopropyl)$; 1.26/t J=6, $CH_3(ester)$; 3.17/m γ -H; 5.68/s 2-H; 4.12/q J=6, $CH_2(ester)$; 7.17/m ArH. For (Z): 0.66/m $-CH_2CH_2-(cyclopropyl)$; 0.98/t J=6, $CH_3(ester)$; 1.70/m γ -H; 3.85/q J=6, $CH_2(ester)$; 5.71/s 2-H; 7.17/m ArH.

Ethyl (E+Z)-2-methyl-3-phenyl-3-cyclopropylacrylates (78)

A mixture of esters 78 (E:Z ~ 1:2), b.p. 100-105°/0.2 Torr, was obtained from cyclopropyl phenyl ketone (76) with phosphonopropionate.

UV: 238 (5400) for (E), 210 (9300) for (Z). IR: 1735 s for (Z), 1720 s for (E).

MS: 230 ($C_{15}H_{18}O_2^+$), 202, 157. NMR; CCl_4 : for (Z): 0.30/m $-CH_2CH_2-$ (cyclopropyl); 0.68/t J=7, CH_3 (ester); 1.82/m γ -H; 2.16/s 2- CH_3 ; 3.68/q J=7, CH_2 (ester); 7.07/m ArH. For (E): 1.22/t J=7, CH_3 (ester); 1.30/m $-CH_2CH_2-$ (cyclopropyl); 1.58/s 2- CH_3 ; 2.66/m γ -H; 4.20/q J=7, CH_2 (ester); 7.07/m ArH.

3-(1-Phenylcyclopropyl)-acrylic acid (64)

To 4.3 g (42.3mmol) of malonic acid in 50 ml of pyridine were added 4.0 g (27.4mmol) of 61 and 2 ml of piperidine. The mixture was heated at 100° for about 2 h until all CO_2 was evolved. The solution was then poured onto 2N sulfuric acid and extracted in the usual way. Recrystallization from ether/hexane gave 3.5 g (68%) of the (E)-acid; m.p. 134°.

IR; $CHCl_3$: 3500-2500 m broad, 1695 s, 1638 m. MS: 188 ($C_{12}H_{12}O^+$), 143, 128. NMR: 1.26/m $-CH_2CH_2-$ (cyclopropyl); 5.27/d J=15, 2-H; 5.75/d J=15, 3-H; 7.28/s ArH.

Hydrolysis of the esters 62, 63, 72, 77, and 78

The esters were stirred in a 1:1 mixture of 20% methanolic potassium hydroxide solution and water until a homogeneous solution was formed. After acidification with 10% sulfuric acid and work-up, the acids were recrystallized from hexane with a small amount of methylene chloride.

2-(1-Phenylcyclopropyl)-acrylic acid (64)

3.0 g of (E)-62 afforded 1.9 g (73%) of acid (E)-64; m.p. 131°. Spectral data see above.

(E)-2-Methyl-3-(1-phenylcyclopropyl)-acrylic acid (65)

2.0 g of (E)-63 gave 1.4 g (80%) of acid (E)-65; m.p. 90°.

IR: CHCl_3 : 3600-2700 m broad, 1692 s. MS: 202 ($\text{C}_{13}\text{H}_{14}\text{O}_2^+$), 174, 157. NMR:

1.15/m $-\text{CH}_2\text{CH}_2-(\text{cyclopropyl})$; 1.60/d $J=1$, 2- CH_3 ; 6.95/q $J=1$, 3-H; 7.15/s ArH.

(E)-3-(1-Phenylcyclopropyl)-2-butenic acid (73)

3.0 g of (E)-72 afforded 2.0 g (75%) of acid (E)-73; m.p. 99°.

IR; CHCl_3 : 3600-2800 m broad, 1695 s, 1645 m. MS: 202 ($\text{C}_{13}\text{H}_{14}\text{O}_2^+$), 174, 157. NMR: 1.15/m $-\text{CH}_2\text{CH}_2-(\text{cyclopropyl})$; 2.10/d $J=1$, CH_3-4 ; 5.78/q $J=1.5$, 2-H; 7.28/s ArH.

(E+Z)-3-Phenyl-3-cyclopropylacrylic acid (79)

1.0 g (80%) of acids (E+Z)-79, m.p. 110°, were obtained from 1.5 g of esters (E+Z)-77.

IR; CHCl_3 : 3500 w, 3400-2800 m broad, 1692 s, 1632 m. MS: 188 ($\text{C}_{12}\text{H}_{12}\text{O}_2^+$), 160, 143. NMR; for (Z): 0.70/m $-\text{CH}_2\text{CH}_2-(\text{cyclopropyl})$; 1.75/m γ -H; 5.77/s 2-H; 7.15/m ArH. For (E): 0.50/m $-\text{CH}_2\text{CH}_2-(\text{cyclopropyl})$; 3.10/m γ -H; 5.70/s 2-H; 7.15/m ArH.

(E)-And(Z)-2-methyl-3-phenyl-3-cyclopropylacrylic acids (80)

Hydrolysis of (E)- and (Z)-78 gave acids (E)- and (Z)-80 with m.p. 138° and 134°, respectively.

IR; CHCl_3 : 3500 w, 3400-2700 m broad, 1685 s, 1600 m. MS: 202 ($\text{C}_{13}\text{H}_{14}\text{O}_2^+$),

174, 157. NMR; for (E): 0.55/m $-\text{CH}_2\text{CH}_2-(\text{cyclopropyl})$; 1.68/s 2- CH_3 ; 3.01/m γ -H; 7.29/m ArH. For (Z): 0.58/m $-\text{CH}_2\text{CH}_2-(\text{cyclopropyl})$; 1.86/m γ -H; 2.15/s 2- CH_3 ; 7.24/m ArH.

Methyl ketones

The acids were dissolved in dry ether and 2.2 eq. of a 2M ether solution of methyl lithium were added under argon. This mixture was refluxed overnight and then hydrolyzed by pouring it onto a large excess of saturated ammonium chloride solution, extracted and purified by column chromatography using Tol-EA 4:1.

(E)-1-(1-Phenylcyclopropyl)-but-1-en-3-one (66)

1.5 g of (E)-64 gave 1.3 g (88%) of (E)-66 after recrystallization from hexane; m.p. 47° .

UV: 313 (100), 240 (14000). IR: 1700 s (s-syn), 1675 s (s-anti), 1620 s. MS: 186 ($\text{C}_{13}\text{H}_{14}\text{O}^+$), 171, 158, 143, 43. NMR; CCl_4 : 1.50/m $-\text{CH}_2\text{CH}_2-(\text{cyclopropyl})$; 2.00/s CH_3 -4; 5.45/d J=15, 2-H; 6.45/d J=15, 1-H; 7.24/m ArH.

(E)-1-(1-Phenylcyclopropyl)-2-methylbut-1-en-3-one (67)

3.7 g of (E)-65 gave 3.5 g (95%) (E)-67 as a slightly yellow viscous liquid.

UV: 313 (120), 240 (15500). IR: 1680 s, 1640 m, 1610 m. MS: 200 ($C_{14}H_{16}O^+$), 185, 172, 157, 43. NMR; CCl_4 : 1.12/m $-CH_2CH_2-(cyclopropyl)$; 1.64/d J=1, 2- CH_3 ; 2.20/s CH_3 -4; 6.70/q J=1, 1-H; 7.10/s ArH.

(E)-2-(1-Phenylcyclopropyl)-pent-2-en-4-one (74)

2.0 g of (E)-73 gave 1.8 g (80%) of (E)-74.

UV: 313 (120) 242 (17500). IR: 1698 s, 1618 s. MS: 200 ($C_{14}H_{16}O^+$), 185, 172, 157, 43. NMR; CCl_4 : 1.05/m $-CH_2CH_2-(cyclopropyl)$; 2.00/d J=1, CH_3 -1; 2.03/s CH_3 -5; 6.00/q J=1, 3-H; 7.16/s ArH.

(E+Z)-1-Phenyl-1-cyclopropylbut-1-en-3-ones (81)

7.7 g of (E+Z)-79 gave 7.4 g (96%) of (E+Z)-81.

UV: 313 (170), 254 (11000). IR: 1685 s for (Z), 1665 s for (E), 1590 s. MS: 186 ($C_{13}H_{14}O^+$), 171, 158, 143, 43. NMR; CCl_4 : 0.65/m $-CH_2CH_2-(cyclopropyl)$; 1.60/s (Z)- CH_3 -4; 2.14/s (E)- CH_3 -4; 1.78/m (Z)- γ -H; 3.20/m (E)- γ -H;

5.96/s (Z)-2-H; 6.02/s (E)-2-H; 7.17/m ArH.

(E+Z)-1-Phenyl-1-cyclopropyl-2-methylbut-1-en-3-ones (82)

3.7 g of (E+Z)-80 gave 3.3 g (90%) of (E+Z)-82.

UV: 313 (150), 252 (17000). IR: 1680 s, for (Z), 1670 s for (E), 1600 m. MS: 200 ($C_{14}H_{16}O^+$), 185, 172, 157, 43. NMR; CCl_4 : 0.52/m $-CH_2CH_2-(cyclopropyl)$; 1.46/s (Z)-2- CH_3 ; 1.58/s (E)-2- CH_3 ; 2.05/s (Z)- CH_3 -4; 2.32/s (E)- CH_3 -4; 7.22/m ArH.

Thermal rearrangement of the cyclopropylvinyl ketones

1-5% Benzene solutions of the ketones were dropped in a nitrogen stream through a column filled with quartz tubes (length and diameter 0.5 cm each) and heated to 350-400°. The vapors were condensed into a flask and the solution was recycled until complete conversion of starting material was attained. The reaction was monitored by VPC. The products were isolated by column chromatography using Tol-EA 4:1.

1-Phenyl-3-acetyl-1-cyclopentene (68)

1.0 g of 66 was pyrolyzed at 400° to give 0.9 g (90%) of 68 as a yellowish viscous liquid.

UV: 366 (13), 340 (35), 313 (630), 300 (1500), 254 (20000). IR: 1717 s, 1605 m.

MS: 186 ($C_{13}H_{14}O^+$), 143, 43. NMR: 2.10/s CH_3 ; 2.45/m $-CH_2CH_2-$; 3.60/m 3-H; 6.10/m 2-H; 7.20/m ArH.

1-Phenyl-3-methyl-3-acetyl-1-cyclopentene (69)

69 was obtained in 50% yield after 6 h of pyrolysis of 67 at 350° (30% of starting ketone was recovered).

UV: 313 (600), 300 (1200), 254 (18000). IR: 1710 s, 1600 m. MS: 200 ($C_{14}H_{16}O^+$), 157, 43. NMR; CCl_4 : 1.25/s 3- CH_3 ; 2.05/s $COCH_3$; 2.63/m $-CH_2CH_2-$; 5.93/m 2-H; 7.25/m ArH.

1-Phenyl-2-methyl-3-acetyl-1-cyclopentene (75)

74 was pyrolyzed at 400° until no starting material was left (2 runs) and gave an almost quantitative yield of 75.

UV: 313 (240), 300 (455), 254 (15000). IR: 1710 s, 1605 m. MS: 200 ($C_{14}H_{16}O^+$), 157, 43. NMR; CCl_4 : 1.68/broad s 2- CH_3 ; 1.96/s $COCH_3$; 2.50/m $-CH_2CH_2-$; 3.41/m 3-H; 7.14/s ArH.

3-Acetyl-2-phenyl-1-cyclopentene (83)

83 was obtained in quantitative yield from 81 after one run at 400°.

UV: 313 (260), 300 (650), 254 (10000). IR: 1715 s, 1590 m. MS: 186 ($C_{13}H_{14}O^+$), 143, 43. NMR; CCl_4 : 1.88/s CH_3 ; 2.49/m $-CH_2CH_2-$; 3.83/m 3-H; 6.28/m 1-H; 7.25/s ArH.

3-Acetyl-3-methyl-2-phenyl-1-cyclopentene (84)

82 gave a 45% yield of 84 after 8 h of pyrolysis at 350° (25% of 82 were recovered).

UV: 313 (80), 300 (180), 254 (10000). IR: 1710 s, 1605 w. MS: 200 ($C_{14}H_{16}O^+$), 157, 43. NMR; CCl_4 : 1.30/s 3- CH_3 ; 2.02/s $COCH_3$; 2.25/m $-CH_2CH_2-$; 6.22/m 1-H; 7.18/s ArH.

Mixture of diastereoisomeric 1-phenyl-3-(1-hydroxyethyl)-1-cyclopenten-2-ones (86)

0.25 g (1.34mmol) of ketone 68 were dissolved in methanol/water 1:1 and 1.5mmol of sodium borohydride were added at 0°. The reaction mixture was stirred at room temperature until no more hydrogen was evolved and then poured onto a saturated ammonium chloride solution and worked up in the usual way.

IR; CHCl_3 : 3620 m, 3520-3120 m broad. NMR; CCl_4 : 1.12/d CH_3 ; 1.60-3.00/m 3-H and $-\text{CH}_2\text{CH}_2-$; 3.70/m 1'-H; 6.10/m 2-H; 7.35/m ArH.

Mixture of diastereoisomeric 1-phenyl-3-(1-acetoxyethyl)-1-cyclopenten-2-ones (87)

The crude alcohols 86 were dissolved in a 1:1 mixture of acetic anhydride and pyridine and stirred at room temperature overnight. After work-up and column chromatography with Tol-EA 4:1 0.15 g of esters 87 were obtained (50% yield from ketone 68).

IR: 1740 s, 1248. NMR: 1.21/d J=6, 1'- CH_3 ; 2.20/m $-\text{CH}_2\text{CH}_2-$; 1.97/s and 2.02/s CH_3CO ; 3.04/m J=9 and 3, 3-H; 4.94/two d of q J=9 and 3, J=6, 1'-H; 6.08/m 2-H; 7.33/m ArH.

4.3 Direct Irradiation of the Acetylphenylcyclopentenes

4.3.1 Qualitative irradiation of 68, 69, 75 and 84

0.2 M Degassed benzene solutions of the ketones were irradiated at > 300 nm in 2-ml pyrex tubes. Light source: 250 W Hg medium pressure lamp (PHILIPS or MEDA) in a pyrex cooling finger. The reactions were monitored by VPC (15% SE-30/175⁰). After ca. 80 h of irradiation ketones 68 and 69 had disappeared completely and gave rise to one sole photoproduct each. 75 and 84 remained unchanged after ca. 100 h. NMR analysis of the crude reaction mixtures after evaporation of solvent showed in the case of 68 and 69 the isomeric ketones 92 and 97 (cf. spectral data below), and in the case of 75 and 84 only starting material was observed.

4.3.2 Preparative irradiation of 68 and 69

1-Phenyl-1-acetyl-2-cyclopentene (92)

A ca. 0.05 M degassed solution of 1.0 g of 68 in 150 ml of ether was irradiated in a quartz tube at 254 nm with a Hg low pressure lamp. The reaction was monitored by VPC. After 3 h the starting material had completely disappeared. Purification by column chromatography with Tol-EA 4:1 gave ketone 92 in 52% yield.

UV: 313 (270), 300 (590), 258 (1400). IR: 1712 s, 1603 m. MS: 186 ($C_{13}H_{14}O^+$), 143, 43. NMR; 2.45/m $-CH_2CH_2-$; 2.01/s CH_3 ; 6.10/s CH-2 and -3 (in C_6D_6 : 5.80/m); 7.36/m ArH.

1-Methyl-3-acetyl-3-phenyl-1-cyclopentene (97)

A 0.04 M degassed solution of 0.40 g of 69 in 50 ml of benzene was irradiated at > 300 nm in a pyrex tube. After ca. 75 h all starting material was gone and 97 was collected by VPC (15% SE-30, 175°) in ca. 30% yield.

IR: 1715 s, 1610 m. MS: 200 ($C_{14}H_{16}O^+$), 157, 43. NMR; CCl_4 : 1.80/d $J=1$, 1- CH_3 ; 1.86/s $COCH_3$; 1.92-2.68/m $-CH_2CH_2-$; 5.60/q $J=1$, CH-2; 7.12/m ArH.

4.3.3 Synthesis of 1-Phenyl-1-acetylcyclopentane (93)

a) 0.1 g of 92 was hydrogenated with a catalytic amount of Pd/C in 15 ml of ethyl acetate. The mixture was stirred at room temperature overnight. The catalyst was then filtered off and the solvent evaporated. A quantitative yield of 93 was obtained; m.p. 138°.

UV: 313 (80), 300 (250), 254 (290). IR: 1710 s. MS: 188 ($C_{13}H_{16}O^+$), 145, 43. NMR: 1.70/m (6H); 1.86/s CH_3 ; 2.51/m (2H); 7.13/s ArH.

b) 93 was also prepared by hydrolysis of 1-phenyl-cyclopentane-1-carbonitrile (95)²⁹ followed by treatment of the acid 96 with methyl lithium:

1.0 g of 95 was refluxed in a 1:1 mixture of 20% methanolic potassium hydroxide solution and water until a homogenous solution was formed. Acidification with 10% sulfuric acid and work-up gave 1-phenyl-cyclopentane - carboxylic acid (96) in 50% yield; m.p. 150°.

IR: 3500-2500 broad m, 1702 s. MS: 190 ($C_{12}H_{14}O_2^+$), 145. NMR: 1.90/m, (6H), 2.64/m (2H); 7.20/m ArH.

0.9 g (4.7mmol) of acid 92 was dissolved in 40 ml of dry ether. 2.2 eq. of a 2M ether solution of methyl lithium were added under nitrogen. The mixture was refluxed for 5 h and then hydrolyzed and extracted in the usual way. 0.8 g (88%) of ketone 93 was obtained; m.p. 140°.

4.3.4 Photolyses of 92

a) Irradiation of a 0.2M degassed benzene solution of 92 in a pyrex tube at > 300 nm showed after 25 h no trace of 68 by VPC and NMR.

b) A 0.2m nitrogen-purged ether solution of 92 was irradiated in a quartz tube at 254 nm for 25 h. VPC and NMR analysis did not show any detectable amounts of 68 or 98.

4.3.5 Preparation and Irradiation of 92-d₃

3-Phenyl-3-trideuterioacetyl-1-cyclopentene (92-d₃)

300 mg of 92 were dissolved in 12 ml of dioxan and 250 mg of potassium carbonate in 12 ml of D₂O were added. The mixture was stirred at 75° overnight and extracted with ether. The organic phase was washed twice with small amounts of D₂O. Evaporation of the solvent resulted in an almost quantitative yield of 92-d₃.

MS: 189 (C₁₃H₁₁D₃O⁺), 143, 46. NMR: The signal at 2.01 is missing.

Crossing experiment: Irradiation of 68 and 92-d₃

A solution of 50 mg each of ketones 68 and 92-d₃ in 1 ml of benzene was irradiated at > 300 nm. After 60% disappearance of 68 the remaining 68 was collected by VPC (15% SE-30). MS showed admixture of ca. 10% 68-d₃.

MS: 189 (C₁₃H₁₁D₃O⁺)/186 (C₁₃H₁₄O⁺), 143, 46/43.

Crossing experiment: Irradiation of 69 and 92-d₃

A solution of 40 mg each of ketones 69 and 92-d₃ in 1 ml of benzene was irradiated

at > 300 nm. Isolation by VPC of 92-d₃ and 97 after ca. 80% conversion of 69 followed by MS analysis showed exclusively 92-d₃ and 97 (and no 92 and 97-d₃).

4.4 Triplet Sensitization of the Acetylphenylcyclopentenenes 68, 69, 75, 83, and 84

4.4.1 Sensitized Irradiations

a) 0.2M Nitrogen-purged acetone ($E_T \sim 80$ kcal/mol) solutions of 68, 83, 84 and 92 were irradiated at > 300 nm in 2 ml pyrex tubes. The reactions were monitored by VPC (15% SE-30, 175°). After 15 h of irradiation 68 had completely disappeared and no detectable photoproduct could be observed by NMR. 83, 84 and 92 remained unchanged with little degradation of starting material after ca. 100 h of irradiation.

b) 0.2M Nitrogen-purged benzene solutions of 68, 69, 75, 83 and 84 each sensitized with 1 eq. of benzophenone ($E_T=69$ kcal/mol), were irradiated at 366 nm (366 glass tube filter) in 2 ml pyrex tubes with a 250 W Hg medium pressure lamp. VPC analysis during photolysis showed only one photoproduct with each of 68, ($\rightarrow$ 98a,b), 69 ($\rightarrow$ 119) and 75 ($\rightarrow$ 120a,b). 83 and 84 remained unchanged which was also confirmed by NMR analysis of the crude reaction mixtures.

c) A 0.2M nitrogen-purged solution of 68 in neat acetophenone ($E_T=74$ kcal/mol) was irradiated at > 300 nm. Complete conversion after ca. 7 h. VPC isolation of the photoproduct followed by NMR analysis resulted in an inseparable ca. 3:1 endo-exo mixture of 98a,b.

d) Sensitized irradiations at 366 nm were carried out with 0.2M nitrogen-purged benzene solutions of 10 g of 68 with 0.1 eq. each of thioxanthone ($E_T=65$ kcal/mol) and Michler's ketone ($E_T=62$ kcal/mol) and gave full conversions to 98 after ca. 6 h. Isolation of 98 by column chromatography using Tol-EA 4:1 resulted in both cases in a 65% yield of 98a,b (ca. 3:1 endo-exo ratio by NMR).

e) Sensitized irradiation of 40 mg of 68 with 5 eq. of racemic indanone 139 ($E_T=74$ kcal/mol) in 2 ml of nitrogen-purged benzene at 366 nm resulted also in the appearance of 98 (VPC; coinjection with authentic 98).

f) Irradiation at 366 nm of 0.2M nitrogen-purged benzene solutions of 68 with 2 eq. of α - and β -acetophenone ($E_T=56$ and 59 kcal/mol, respectively) resulted in no sensitization. After 50 h of irradiation only starting ketone 68 could be detected.

4.4.2 Photoproducts

endo- And exo-1-phenyl-5-acetylbicyclo[2.1.0]pentanes (98a,b)

98a,b were isolated by VPC. The 3:1 endo-exo mixture could not be separated. VPC coinjection with a synthetically prepared endo-exo mixture of 98 gave rise to one single peak.

IR: 1720 s for endo; 1705 s for exo. NMR; CCl_4 : 1.50-2.70/m CH_2 -2 and -3, CH-4 and -5; 1.80/s exo- CH_3 ; 2.18/s endo- CH_3 ; 7.10/m ArH (see below for structure proof and additional data).

endo-1-Phenyl-4-methyl-5-acetylbicyclo[2.1.0]pentane (119)

The NMR spectrum of the crude reaction mixture shows 1.30/s 4- CH_3 ; 1.70-2.50/m CH_2 -2 and -3, CH-5; 2.17/s COCH_3 ; 7.02/m ArH.

endo-And exo-1-phenyl-5-acetyl-5-methylbicyclo[2.1.0]pentanes (120a,b)

The NMR spectrum of the crude reaction mixture shows a 1:1 ratio of 120a+b: 1.47/s exo-5- CH_3 ; 1.53/s endo-5- CH_3 ; 1.60-2.30/m CH_2 -2 and -3, CH-4; 2.02/s exo- and endo- COCH_3 ; 7.05/m ArH.

4.4.3 Irradiation of 98a and 98b

0.2M solutions of 98a and 98b, each sensitized with 1 eq. of benzophenone in

benzene at 366 nm, in neat acetophenone and in acetone at > 300 nm in 1 ml pyrex tubes did not lead to any interconversion. In the presence of benzo-phenone 98a and 98b remained unchanged, but in acetophenone and acetone they were slowly consumed without appearance of other protoproducts.

4.4.4 Synthesis of 98a and 98b

Ethyl endo- and exo-1-phenylbicyclo[2.1.0]pentane-5-carboxylates (101a,b)

To 1.2 g of 100, prepared by the method of Bennet and Burger⁴⁵, and 70 mg of dry CuSO_4 were added consecutively 3 portions of 0.5 eq. of ethyl diazoacetate. Nitrogen vigorously evolved upon each addition. The mixture was kept at ca. 40° and the reaction was monitored by TLC with Tol-EA 4:1. After full conversion of starting material (side products: maleate and fumarate) the reaction mixture was filtered. Column chromatography (Tol-EA 4:1) gave 0.4 101a and 0.6 g 101b. Total yield 63%.

101a UV: 313 (9), 276 (120), 267 (260), 260 (440), 253 (600), 248 (850), 220 (4100). IR: 3065 m, 3035 m, 2985 m, 2955 m, 1735 s, 1610 m, 1435 m, 1325 m, 1250 m, 1170 s, 1125 m, 697 m. MS: 216 ($\text{C}_{14}\text{H}_{16}\text{O}_2^+$), 171, 143, 128. NMR; CCl_4 : 1.25/t J=7, CH_3 ; 1.90-2.50/m CH_2 -2 and -3, CH-4 and -5; 4.10/q J=7, CH_2 (ester); 7.15/m ArH.

101b UV: identical with UV of 101a. IR: 3070 m, 3040 m, 2990 m, 2940 m, 1730 s, 1610 m, 1375 m, 1350 m, 1260' m, 1165 s, 700 m. MS: identical with MS of 101a. NMR; CCl_4 : 0.90/t J=7, CH_3 ; 1.42-2.60/m CH_2 -2 and -3, CH-4 and -5; 3.80/q J=7, CH_2 (ester); 7.15/m ArH.

endo- And exo-1-phenylbicyclo[2.1.0]pentane-5-carboxylic acids (102a,b)

0.4 g of 101a and 0.6 g of 101b were hydrolyzed separately as described above for 62 etc. Recrystallization from hexane/ CH_2Cl_2 resulted in 0.33 g of 102a, m.p. 110° , and 0.52 g of 102b, m.p. 131° .

102a IR; CHCl_3 : 3500 w, 3400-2500 m broad, 1705 s, 1608 m, 1450 m, 1140 m, 1110 m. MS: 188 ($\text{C}_{12}\text{H}_{12}\text{O}_2^+$), 170 143, 128. NMR: 2.00-2.65/m CH_2 -2 and -3, CH-4 and -5; 7.20/m ArH.

102b IR; CHCl_3 : 3500 w, 3400-2500 m broad, 1698 s, 1608 w, 1445 m, 1130 m. MS: identical with MS of 102a. NMR: 1.50-2.65/m CH_2 -2 and -3, CH-4 and -5; 7.18/s ArH.

endo- And exo-1-phenyl-5-acetylbicyclo[2.1.0]pentanes (98a,b)

Treatment of 0.3 g and 0.5 g of 102a and 102b with 2.2 eq. of methyl lithium

each gave, after isolation by column chromatography (Tol-EA 4:1) 200 mg (67%) of 98a and 230 mg (48%) of 98b.

98a UV: 348 (53), 323 (150), 313 (250), 300 (400), 292 (500), 262 (3000), 252 (4000), 220 (9400), 210 (11000). IR: 3070 m, 3040 m, 3000 m, 2950 m, 1710 s, 1608 m, 1500 m, 1420 m, 1355 m, 1250 m, 1165 m, 695 m. MS: 186 ($C_{13}H_{14}O^+$), 143, 128. NMR: 1.90-2.70/m CH_2 -2 and -3, CH-4 and -5; 2.28/s CH_3 ; 7.22/m ArH.

98b UV: identical with UV of 98a. IR: 3060 m, 3035 m, 2980 m, 2940 m, 1705 s, 1608 m, 1500 m, 1435 m, 1365 m, 1245 m, 1175 m, 698 m. MS: identical with MS of 98a. NMR: 1.50-2.70/m CH_2 -2 and -3, CH-4 and -5; 1.96/s CH_3 ; 7.24/s ArH.

4.4.5 Quantum Yield Measurements for 68

The quantum yields of consumption, Φ_{-68} , and product formation, Φ_{92} and Φ_{98} , were determined in benzene solutions (except for run 2) at 20° using an electronically integrating actinometer⁷⁷. The product compositions were analysed by gas chromatography with dodecane or tridecane as an internal reference on a $1/4'' \times 10'$ steel column packed with 15% SE-30 on Chromosorb W-HP at 175° in connection with an electronic integrator INFRATRONICS CRS-208. Under these VPC conditions the thermal rearrangement of 98 to starting ketone 68 is negligible. The Φ values given were averaged from multiple measurements at each of several

different conversions within the range indicated in Table III. Estimated experimental error, runs 1-5: $\pm 10\%$; runs 6 and 7: $\pm 30\%$. Results see Table III, page 63.

4.5. Emission Spectroscopy and Quantum Yields of Phosphorescence of 1-Phenyl-3-acetyl-1-cyclopentene (68) and 1-Phenylcyclopentene (91)

The emission spectra of 68 and 91 were measured on a modified FICA 55 spectrophotometer at 77K in EPA (ether/isopentane/ethanol 5:5:2). Diameter of sample tube 2 mm; light source XBO-450 W high-pressure Xe lamp; photomultiplier R 106; spectral resolution 5 and 2,5 nm. The phosphoroscope has been designed in our laboratory (now commercially available from Holzer Instrumentation scientifique, Lausanne) and its mechanical construction is similar to that described by Wild et al.⁷⁸. The stepwise operation of the shutter cylinder is controlled by an electronic quartz time base; invariable delay time between entrance and exit phase 7 ms; the cylindrical shutter can be removed from the light path. The spectra were run on one-channel operation mode (noncorrected) at repetition intervals of 40 or 100 ms. Phosphorescence lifetimes were measured by external synchronization of the shutter with an oscilloscope (Tektronix, Type 564B 3A6 3B4); internal synchronization of a camera with the oscilloscope photographed the relaxation curve.

For the determination of the quantum yields of phosphorescence in EPA at 77K

the shutter was removed and the emission spectra were recorded linearly in wave-numbers and intensity corrected on two-channel (rhodamine B) operation mode. Solutions of $T \geq 90\%$ at $d=1$ mm and of similar extinctions at the excitation wavelength (310 nm) were used. Spectral integration was carried out gravimetrically, i.e. by cutting and weighing of the peaks. As a reference for Φ_p of 68 and 91 served the value of β -acetophenone ($\Phi_p=0.05$). Estimated experimental error: $\pm 5\%$ for 68 and $\pm 50\%$ for 91.

4.6. Thermolysis of 1-Phenyl-5-acetylbicyclopentanes (98a,b)

5% Nitrogen-purged deuteriobenzene solutions of 98a and 98b in sealed NMR tubes were thermolyzed at 100° for 3 h and then for another 10 h at 140° in an oil bath. At certain time intervals the NMR spectra of the two samples were recorded. The composition of the mixtures of 98a, 98b and 68 during the course of the thermolysis was determined by NMR integration of the methyl ketone peaks. These compositions are represented in Figures 4 and 5 and Table IV, page 72. VPC analysis of the two mixtures after evaporation of the solvent confirmed the NMR results, i.e. ca. 75% of 68 and ca. 25% of 98a + 98b. The endo- and exo-bicyclopentanes could not be separated by VPC.

4.7. Synthesis of (1S, 4R, 4aS, 9aS)-(-) and (1R, 4S, 4aR, 9aR)-(+)-1,2,3,4,4a, 9a-Hexahydro-1, 4-methanofluoren-9-one (139)

(±)-endo-1,4,4a,9a-Tetrahydro-1,4-methanofluoren-9-one (138)

To 5.0 g (0.04mol) of indenone (137)⁶⁹ in 50 ml of benzene were added 6.4 g (0.04mol) of freshly distilled cyclopentadiene. The mixture was refluxed for three h and the benzene was then evaporated. The crude product was filtered through neutral aluminum oxide, activity III, and column-chromatographed on silicagel with Tol-EA 4:1 to give 7.1 g (93%) of 138; m.p. 57-58°.

UV: 367 (10), 351 (20), 342 (24), 335 (25), 327 (27), 313 (23), 294 (2350), 285 (2050), 245 (8700), 240 (10500), 212 (11000). IR: 3080 m, 2985 m, 2880 m, 1720 s, 1610 m, 1470 m, 1345 m, 1345 m, 1290 m, 1140 m, 688 m. MS: 196 ($C_{14}H_{12}O^+$), 131, 130, 102, 66. NMR: 1.69/d+1.81/d $J_{AB}=12$, $-CH_2-$; 3.06-3.82/m 1-H, 4-H, 9a-H; 3.86/dd $J_{4a9a}=6.0$, 4a-H; 5.44/q $J=5.5$, 2-H; 5.86/q $J=5.5$, 3-H; 7.45/m ArH; (for structure proof see p. 85).

(±)-1,2,3,4,4a,9a-Hexahydro-1,4-methanofluoren-9-one (139)

Catalytic hydrogenation was effected with 7.0 g of 138 on 0.7 g of 10% Pd/C in 70 ml of ethyl acetate under stirring at room temperature for 24 h. Filtration through celite, evaporation of the solvent and recrystallization from methylene

chloride/hexane gave 6.4 g (90%) of 139; m.p. 60°.

UV: 370 (7), 353 (18), 346 (24), 340 (26), 330 (29), 317 (25), 293 (3150), 284 (2900), 271 (1850), 247 (14000), 239 (15000), 209 (27000). IR: 3080 m, 3040 m, 2970 s, 2890 m, 1720 s, 1612 m, 1470 m, 1290 m, 1230 m, 695 m. MS: 198 ($C_{14}H_{14}O^+$), 132, 131. NMR: 1.10-1.90/m three $-CH_2-$; 2.60-2.80/m 1-H, 4-H; 2.96/dd $J_{4a,9a}=8.0$, $J_{1,9a}=5.0$, $J_{2,9a}=1.0$, 9a-H; 3.68/dd $J_{4,4a}=5.0$, $J_{3,4a}=0.5$, 4a-H; 7.50/m ArH.

(±)-endo-1,4,4a,9a-Tetrahydro-1,4-methanofluoren-endo-9-ol (140)

20.0 g (0.1mol) of ketone 138 were dissolved in 100 ml of methanol and 5.0 g (0.13mol) of sodium borohydride were added to 6.0 ml 2N sodium hydroxide and 54 ml of water. The reaction mixture was stirred at room temperature overnight and then poured onto saturated NH_4Cl solution. The usual work-up and recrystallization from CH_2Cl_2 /hexane gave 140 in 95% yield (19.2 g); m.p. 124-126°.

IR: 3600 m. MS: 198 ($C_{14}H_{14}O^+$), 197, 130. NMR: 1.57/d+1.65/d $J=10$, $-CH_2-$; 3.05-3.40/m 1-H, 4-H, 9a-H; 3.86/dd 4a-H; 5.18/broad d $J_{9,9a}=9.0$, 9-H; 5.52/q $J=5.2$, 2-H; 6.06/q $J=5.2$, 3-H; 7.24/m ArH.

(±)-1,2,3,4,4a,9a-Hexahydro-1,4-methanofluoren-endo-9-ol (141)

Reduction of 139 as above gave 141 in 50% yield; m.p. 90-92°.

IR: 3640 m. MS: 200 ($C_{14}H_{16}O^+$), 199, 132, 116. NMR: CCl_4 : 0.80-1.60/m three $-CH_2-$; 2.34-2.64/m 1-H, 4-H; 2.90/dd 9a-H; 3.40/dd 4a-H; 5.22/broad d $J_{9,9a}=9.0$, 9-H; 7.20/m ArH.

(±)-1,2,3,4,4a,9a-Hexahydro-1,4-methanofluoren-exo-9-ol (142)

A mixture of 3.26 g of aluminum isopropoxide and 0.8 g of 139 in 15 ml of toluene was refluxed for 4 h. After cooling 15 ml of isopropanol were added and the acetone formed was distilled off. Column chromatography with Tol-EA 4:1 followed by recrystallization from hexane/ CH_2Cl_2 yielded 80% (0.65 g) of 142; m.p. 110°.

IR: 3620 m. MS: identical with that of 141. NMR: CCl_4 : 0.50-1.70/m three $-CH_2-$; 2.50-3.05/m 1-H, 4-H, 9a-H; 3.80/m 4a-H; 5.15/broad s $J_{9,9a}=0$, 9-H; 7.40/m ArH.

Optical resolution of ($\pm$)-endo-alcohol 140

To a solution of 5.0 g (25mmol) of ($\pm$)-140 in 100 ml of pyridine were added 6.5 g (30mmol) of (-)-camphanic acid chloride⁷⁰. The mixture was stirred overnight and extracted in the usual way after evaporation of most of the pyridine to give 8.6 g (90%) of a mixture of the (+)- and (-)-esters 145. Column chromatography with Tol + 3% of ether resulted in separation and isolation of (+)-145, m.p. 155°, $[\alpha]_D^{20}=+87.76^\circ$ (c=0.2 in CHCl_3), and (-)-145, m.p. 159°, $[\alpha]_D^{20}=-88.58^\circ$ (c=0.2 in CHCl_3).

IR: 1790 s; 1728 s for (+)-145; 1745 s for (-)-145. MS: 378 ($\text{C}_{24}\text{H}_{26}\text{O}_4^+$), 312, 115 (the same for both diastereoisomeric esters). NMR; (+)-145: 1.05/s (3H) + 1.15/s (6H), CH_3 ; 1.55/d + 1.63/d $J=10$, CH_2 -bridge; 2.19/m $-\text{CH}_2\text{CH}_2-$; 2.93/m 4-H; 3.20/m 1-H; 3.42/m 9a-H; 3.88/q $J_{4,4a}=4.5$, $J_{4a,9a}=8$, 4a-H; 5.44/q $J_{2,3}=5.5$, $J_{1,2}=2.7$, 2-H; 6.02/q $J_{2,3}=5.5$, $J_{3,4}=2.5$, 3-H; 6.21/d $J_{9,9a}=10$, 9-H; 7.18/m ArH. (-)-145: 1.12/s (3H) + 1.16/s (6H), CH_3 ; 1.57/d + 1.65/d $J=10$, CH_2 -bridge; 2.20/m $-\text{CH}_2\text{CH}_2-$; 2.92/m 4-H; 3.22/m 1-H; 3.45/m 9a-H; 3.90/q $J_{4,9a}=8$, $J_{4,4a}=4.5$, 4a-H; 5.47/q $J_{2,3}=5.5$, $J_{1,2}=2.7$, 2-H; 5.96/q $J_{2,3}=5.5$, $J_{3,4}=2.5$, 3-H; 6.05/d $J_{9,9a}=9$, 9a-H; 7.20/m ArH.

The diastereoisomeric esters (+)-and (-)-145 showed an optical purity of 92% by NMR, using partly a gravimetrical method, i.e. cutting and weighing of the peaks, and partly electronic peak integration.

The esterification was also carried out with the saturated endo- and exo-alcohols 141 and 142:

To 180 mg (0.9mmol) of 141 in 5 ml of pyridine were added 182 mg (1mmol)

of(-)-camphanic acid chloride. No ester was obtained after 24 hours of stirring at 50°.

80 mg (0.4mmol) of 142 in 2.5 ml of pyridine were stirred overnight at 50° with 81 mg (0.45mmol) of (-)-camphanic acid chloride. The ester was obtained in ca. 80% yield, m.p. 139°.

IR; CHCl_3 : 1805 s, 1730 s. NMR; CCl_4 : 0.95/s (3H) and 1.03/s (6H), CH_3 ; 0.60-1.90/m (6H), $-\text{CH}_2-$; 1.90-2.90/m 1-H, 4-H, 9a-H; 3.75/m 4a-H; 6.27/broad s 9-H; 7.35/m ArH.

5.0 g each of (+)-145 and (-)-145 were stirred for 3 days at room temperature in a 1:1 mixture of 20% methanolic potassium hydroxide solution and water. Work-up resulted in a quantitative yield (2.6 g) of the enantiomeric alcohols (+)-140 and (-)-140. Spectral data identical with those of the racemic alcohol. Recrystallization from hexane/ CH_2Cl_2 gave m.p. 136° and 137°, and $[\alpha]_D = +230^\circ$ and -231° , respectively, ($c=0.2$ in CHCl_3).

2.5 g each of (+)-140 and (-)-140 were oxidized with Jones reagent at 0° for 5 min and poured onto ice, extracted with CH_2Cl_2 and column-chromatographed with Tol-EA 4:1. The enantiomeric ketones (+)-138 and (-)-138 were obtained each in 90% yield (2.3 g) after recrystallization from hexane. (+)-138, m.p. 75-76°, $[\alpha]_D = +56.5^\circ$ ($c=0.2$ in CHCl_3); (-)-138, m.p. 75-76°, $[\alpha]_D = -56.4^\circ$ ($c=0.2$ in CHCl_3). Spectral data identical with those of the racemic ketone.

Catalytic hydrogenation as described for ($\pm$)-138 was effected with 2.0 g each of (+)-138 and (-)-138 and resulted in quantitative yields of (+)-139, m.p. 58-60°, $[\alpha]_D = +67.7^\circ$ (c=0.2 in CHCl_3), and (-)-139 m.p. 61-62°, $[\alpha]_D = -68.4^\circ$ (c=0.2 in CHCl_3). For the circular dichroism data see page 88.

4.8. Sensitization Experiment with (1S,4R, 4aS, 9aS)-(-)-1,2,3,4,4a,9a-Hexahydro-1,4-methanofluoren-9-one (139)

A mixture of 200 mg (1.1mmol) of 68 and 5 eq. of (-)-139 in 5 ml of nitrogen-purged benzene was irradiated at 366 nm until ca. 50% conversion of 68.

The products were then separated by column chromatography (hexane/ether 2:1) and 50 mg of 98a were isolated, $[\alpha]_D = -2.92^\circ$ in CHCl_3 . After a second column chromatography with CH_2Cl_2 /ether 20:1 32 mg of 68 were obtained, $[\alpha]_D = -1.80^\circ$.

A similar photolysis was repeated in toluene at -100° . After 24 h of irradiation no conversion of 68 could be detected. From column chromatographic separation (CH_2Cl_2 /ether 20:1) starting material was recovered which showed no optical rotation.

5.

Summary

Compounds 68, 69, 75, 83 and 84 were synthesized in order to study the photochemical behaviour under direct and triplet-sensitized irradiation conditions. Upon direct photolysis 1-phenyl-3-acetyl-1-cyclopentene (68) undergoes apparently complete isomerization to the 1,3-acetyl shifted product 92. An experiment with appropriate deuterium labels showed that in fact a photostationary equilibrium of ca. 20:1 in favor of 92 is established. Triplet sensitization of 68 afforded a ca. 3:1 mixture of the ODPM rearranged endo- and exo-1-phenyl-5-acetylbicyclo[2,1,0]pentanes (98). The sensitization quantum yields of product formation at room temperature are independent of sensitizer energy in the range of 61 - 74 kcal/mol and drop to zero with a sensitizer of $E_T = 59$ kcal/mol. On the basis of this result and the comparison of the phosphorescences at 77K of 98 and 1-phenylcyclopentene (91) the reactive triplet state of 68 is identified as the localized styrene π, π^* -state of $E_T = 59$ kcal/mol. This constitutes the first experimentally well documented proof of a reactive π, π^* triplet in ODPM rearrangements. The 1-phenyl-5-acetylbicyclopentanes (98) undergo facile thermal endo-exo interconversion and cyclopropyl-allylic rearrangement. The latter affords exclusively the corresponding 1-phenyl-3-acetylcyclopentene (98 $\rightarrow$ 68). The result of these preliminary experiments indicates a general similarity to the thermal isomerization of the acetylbicyclopentanes lacking phenyl substitution as established in detail elsewhere. The only variance appears in the rearrangement which differs strongly in regioselectivity from the previously studied acetyl-

bicyclopentane series.

Investigation of 69, 75, 83 and 84 showed that the photolytical behaviour of these ketones exhibits a strong dependence on the substitution pattern. This study requires further experimentation before meaningful conclusions can be drawn.

The optically active indanone adduct 139 was synthesized and asymmetrically induced sensitization of 68 was attempted. However, no important diastereoisomeric selectivity in the exothermic triplet-triplet transfer was observed. Our hypothesis that the topological matching of the chromophoric moieties of 68 and 139 would result in a noticable optical induction could not be substantiated.

6.

Résumé

Les composés acétylphénylcyclopenténiques 68, 69, 75, 83 et 84 ont été synthétisés dans le but d'étudier leur comportement photochimique dans des conditions d'irradiations directes et sensibilisées.

Par photolyse directe, le 1-phényl-3-acétyl-1-cyclopentène (68) subit une migration d'ordre-1,3 du groupe acétyle apparemment complète. La réaction effectuée sur un produit marqué au deutérium montre qu'un équilibre photo-stationnaire d'environ 20:1 s'établit en faveur du produit réarrangé (92).

L'irradiation sensibilisée du dérivé 68 donne un mélange de produits de réarrangement ODPM endo- et exo-1-phényl-5-acétylbicyclo[2,1,0]-pentanes (98) dans un rapport 3:1. Les rendement quantiques des produits formés par irradiation sensibilisées à température ambiante sont indépendants de l'énergie du sensibilisateur tant que l'on se trouve entre 61 et 74 kcal/mole, mais ils tombent à zéro lorsque cette énergie n'est que de 59 kcal/mole. Ce résultat, ainsi que la comparaison des phosphorescences de 68 et du 1-phényl-cyclopentène (91) à 77K indiquent que l'état triplet réactif de 68 est l'état π, π^* localisé du styrène d'énergie triplet $E_T=59$ kcal/mole. Ceci constitue la première preuve expérimentale de l'existence d'un état réactif triplet- π, π^* dans le réarrangement ODPM.

Le 1-phényl-5-acétylbicyclopentane (98) donne lieu aisément par voie thermique à une interconversion endo-exo ainsi qu'à un réarrangement cyclopropyle-allyle. Ce dernier produit uniquement le 1-phényl-3-acétylcyclopentène (98 $\rightarrow$ 68) correspondant. Le résultat de ces expériences préliminaires montre qu'au cours

de l'isomérisation thermique, nos composés se comportent de façon analogue aux dérivés acétylbicyclopentanes non-phénylés étudiés ailleurs. La seule divergence notable apparaît dans la régio-sélectivité du réarrangement cyclopropyl-allyle.

Le présent travail sur les dérivés acétylphénylcyclopentènes 69, 75, 83 et 84 a montré que le comportement photochimique de ces cétones est étroitement dépendant de la nature des substituants. Cependant, une recherche plus approfondie s'avère nécessaire pour pouvoir tirer des conclusions significatives. Le dérivé optiquement actif de l'indanone (139) ($E_T=74$ kcal/mole) a été synthétisé et utilisé pour tenter l'induction asymétrique sensibilisée de 68. Cependant, aucune sélectivité diastéreoisomérique importante au cours du transfert triplet-triplet n'a été observée. Notre hypothèse, selon laquelle une concordance topologique des chromophores de 68 et 139 résulterait en une appréciable induction optique, n'a pas été confirmée.

7.

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